

**INHIBITION OF THE PHOTO-INDUCED  
REVERSION OF HIGH-YIELD PULPS  
AND MODEL LIGNIN COMPOUNDS BY  
MERCAPTANS**

by

**Vicky Gail Barnett, B.Sc., (Hons.)**

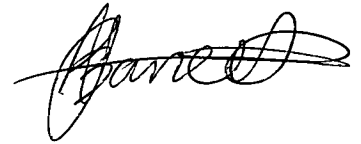
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# DECLARATIONS

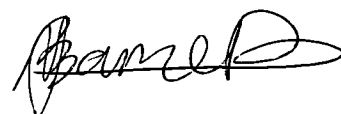
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# ABSTRACT

Lignin-rich pulps, like TMP, have been limited to the manufacture of short-life papers like newsprint. This is because the lignin in these pulps tends to yellow rapidly and extensively when exposed to sunlight (reversion). Researchers have attempted to inhibit this reversion. Some mercaptans exhibit excellent inhibition abilities, but little is known about the mechanism. This thesis explores the inhibition of photo-induced reversion of TMP and model lignin compounds (MLCs) using mercaptans, along with some mechanisms for this inhibition.

Inhibition studies required a quick and accurate simulation of the natural reversion process. Ultraviolet sunlamps were shown to induce rapid photo-reversion of TMP and peroxide bleached TMP (BTMP) handsheets, closely matching sunlight-induced reversion.

Mercaptans, particularly ethylene glycol bithioglycolate (EGB), efficiently inhibited this reversion. Their initial bleaching effect resembled hydrogen peroxide bleaching, possibly via removal of coniferaldehyde structures. Inhibition required the mercaptans to remain within the paper sheet during irradiation, and for *unbleached* TMP results indicated that this inhibition occurred mainly via a removal of yellow irradiation products as they were formed.

Studies on model lignin compounds (MLCs) extended knowledge of both reversion processes, and modes of mercaptan inhibition. Studies confirmed that a free phenolic hydroxyl group was essential for reversion. A C=C or C=O group, in conjunction with the phenolic hydroxyl group, may have sensitised reversion. When C=C and C=O groups were *conjugated* on a side chain, however, reversion was found to be blocked (e.g. 3-methoxy-4-hydroxy cinnamaldehyde).

Mercaptan inhibition of photo-induced reversion in MLCs was shown to be diverse. While some MLCs were completely inhibited (e.g. guaiacol), others were only partially inhibited (e.g. vanillin), or not inhibited at all (e.g. eugenol). For compounds containing a side chain C=C-C=O conjugation (e.g. 3-methoxy-4-hydroxy cinnamaldehyde), mercaptan treatment actually *enabled* reversion, by destroying the conjugation which had previously blocked reversion.

This diversity in MLC inhibition suggests that mercaptans are likely to inhibit via several modes, which are determined by interacting species. This was confirmed by different mechanistic studies. For example, three mercaptans had a strong potential to inhibit

reversion of isoeugenol mainly by removing coloured products of irradiation as they formed. For methoxyhydroquinone and acetovanillone, such a mechanism was supported in only two mercaptans, while for other MLCs (e.g. vanillic acid) this mechanism was possible only as a partial mode of inhibition.

An alternative mode was also found to occur. This involved an inhibition of photo-sensitising reactions, and results again reflected a diversity in effectiveness. For example, while two photo-sensitisers (acetophenone and acetoveratrone) sensitised and enhanced photo-reversion of guaiacol, EGB inhibited only one of these photo-sensitisers (acetoveratrone).

A third mechanism was also demonstrated, which involved a "UV-shielding" effect. Here, the mercaptan did not require contact with the MLC to inhibit reversion. Again, results were varied. Whereas each mercaptan shielded vanillin, no mercaptan shielded guaiacol. Furthermore, EGB shielded methoxyhydroquinone, but the other two mercaptans did not.

Thus, the inhibition of reversion by mercaptans was shown to be a complex process, involving several different modes of action, which are prevalent or not, depending on both the mercaptan and the species it is inhibiting.

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-At my first conference (organised by Appita) I had a great time, and many people took the time to congratulate and compliment me on my presentation. One man even showed enough interest in my talk, to debate its worth! This was such a thrill, and boosted my confidence a great deal. As I was very nervous at the time, sadly I have forgotten many names, but I reassure you that your actions will always be remembered.

It is professionals like those that I mentioned who create a welcoming and encouraging atmosphere for a newcomer in the field, and give us something to aspire to. Your gestures were gratefully received and will never be forgotten.

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# **PREFACE**

I dedicate this thesis to my mum, my dad, my sister, and my brother - because you are all my true inspiration.

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# **CHAPTER 1**

## **INTRODUCTION AND LITERATURE REVIEW**

### **Prologue to Thesis**

This thesis is a contribution to the research currently being undertaken for the resolution of the problem of photo-induced reversion of thermomechanical pulps (TMP). A description of what reversion is, along with reasons as to why it would be advantageous to inhibit it, follow in Section 1.1. An historical overview of the discoveries made into processes involved in photo-induced reversion of mechanical pulps is presented in Section 1.2, and Section 1.3 is a review of the methods previously explored for inhibiting the reversion processes. A brief introduction of parameters used throughout this thesis to monitor photo-induced reversion and its inhibition follow in Section 1.5.

Prior to investigating methods of inhibiting reversion, a reasonable method of reversion induction must be created that is relatively fast, while still representing natural conditions as closely as possible. Chapter 2 describes how this was obtained. The success of mercaptans, particularly thiols, in inhibiting the photo-induced reversion of lignin-rich pulps (see Section 1.3) prompted us to investigate these compounds further. Verification of their inhibition effect on the light-induced reversion of TMP and peroxide bleached TMP (BTMP) handsheets is presented in Chapter 3. Following this, Chapter 4 introduces model lignin compound (MLC) studies in order to clarify which compounds are related to lignin or TMP with respect to their involvement in the photo-yellowing processes, and Chapter 5 determines what type of lignin-related compounds have their photo-reactivity inhibited by the mercaptans studied.

Possible modes of inhibition, i.e. how the mercaptans exert their inhibitory effect, are discussed in Chapter 6 along with experimental evidence to support these claims.

## 1.1 Introduction

### 1.1.1 What is reversion?

Reversion is the term used when pulp or paper discolours from a white bleached state towards, beyond or back to its original state. There are several causes for the reversion of pulp and paper, the main causes being light (photo-induced reversion), heat (thermal-reversion), alkalis (alkali darkening) and natural processes. These are discussed below, with particular emphasis on their effects on high-yield or thermomechanical pulps. Several other factors that may contribute to the yellowing of paper with age include atmospheric conditions (such as temperature, relative humidity and environmental pollutants), paper components (such as lignin, hemicellulose, resin, metal ions and even cellulose itself<sup>1a</sup>) and paper additives (such as rosin, alum, glue and starch<sup>1a</sup>).

#### *Photo-induced or light-induced reversion*

Light-induced reversion is caused by exposure to light, and is both rapid and intense for high-yield pulps (e.g. TMP) and the papers made from them. This is due to their large content of photo-reactive complex lignin molecules. It can occur at room temperature, and depends primarily on the wavelength of the light source, its intensity, time of exposure, and to a lesser degree on temperature, oxygen and relative humidity<sup>2</sup>. Some transition metal ions may also contribute to this discolouration (for example  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ) by photo-sensitising or catalysing the reactions involved, or by creating pigmentation via the formation of coloured complexes or salts, which may give an enhanced yellow appearance<sup>1a,3</sup>. Transition metal ions can, however, be removed from the pulp by chelation, by pre-treating pulps with a chelating agent such as DTPA (sodium diethylenetriaminepentaacetate)<sup>1b</sup>.

There are two main spectral regions photo-reactive to high-yield pulps. The first, the near UV region (in general between 300 and 400nm), has been reported to be responsible for the photo-yellowing or reversion seen in lignin-rich papers<sup>4,5,6,7,8</sup>. This UV light does not penetrate past the top few fibre layers (about 40g/m<sup>2</sup>), and therefore yellowing occurs at paper surfaces only<sup>2</sup>. Longer wavelengths in the visible region of the spectrum (in general between 400 and 600nm) have been found to exhibit a photo-bleaching effect<sup>4,5,6,7</sup>. Unlike photo-reversion, photo-bleaching does penetrate the paper sheet<sup>9</sup>, but it is only a weak action, with the amount of

photo-bleaching being much smaller than that of discolouration<sup>5</sup>. Therefore lignin-rich pulps and papers, under normal sunlight exposure, experience a competition between photo-reversion and photo-bleaching, with the former being much more dominant<sup>4,7,9</sup>.

### ***Thermal reversion***

Thermal reversion occurs at high temperatures, and is largely affected by relative humidity<sup>10</sup>. The resulting discolouration penetrates through the paper sheet. Like light-induced reversion it has been attributed to the presence of lignin in high-yield pulps, but other factors which affect thermal reversion include hydrolysis of hemicellulose, cross-linking reactions, the presence of moisture, and transition metal ions<sup>11</sup>. While some authors believe that thermal reversion reactions are similar to those of light-induced reversion<sup>11</sup>(ref. therein) others believe the two processes are quite distinct<sup>12,13,14</sup>. As thermal reversion requires elevated temperatures, and the resultant colour formation is not as strong as for light-induced reversion of high-yield pulps<sup>11</sup>, it is of less concern with respect to the recessive discolouration of TMP than light-induced reversion.

### ***Alkali darkening***

Alkali darkening is the characteristic darkening of high-yield pulps upon reaction with alkali above pH 10<sup>10</sup>. It is thought to result from similar reactions to those occurring in thermal reversion. The presence of metal ions may increase this type of discolouration<sup>10</sup>. Pre-treatment of pulps with the chelating agent DTPA will remove such harmful metal ions. It is worth noting that despite the alkaline conditions used in hydrogen peroxide bleaching of TMP (about pH 11), alkali darkening is not a major concern. While the peroxide bleaching reactions and alkali darkening processes occur simultaneously, at the alkalinity used in the peroxide bleaching system the bleaching processes dominate and the peroxide stabilises and blocks the alkali darkening by destroying the leucochromophores responsible for this form of discolouration<sup>10</sup>.

### ***Natural aging***

This is the process of natural discolouration that can occur over time, even in the absence of light and heat. Although it may be a possible area of concern from a paper conservator's point of view, its nett effect on the whole of the reversion processes is of little impact with regards to the general paper industry. This is due to

the small extent of this type of reversion over extended periods of time. For example Jordan and co-workers measured the rate of natural aging of newsprint which had been stored in the dark for several years and found a loss of between only 0.4-1.4 ISO brightness units had occurred per year, with an average loss in brightness of about 2% after storage for 2 years<sup>15</sup>. Results cited by Casey showed bleached mechanical pulp sheets, also stored in the dark, again exhibited reasonably good stability, with only a brightness loss of 1.5-2.0 units after three years<sup>16a</sup>.

Of the above types of reversion, light-induced reversion is the predominant cause of recessive discolouration observed in the pulp and paper industry.

### **1.1.2 When did light-induced reversion become a problem and why?**

Light-induced reversion became a major concern after the introduction of wood pulp as a source of paper fibre in the 19th century. Earlier paper makers used linen and cotton fibres which are almost pure cellulose (linen 88%, cotton 95%)<sup>17</sup>. As the popularity of paper increased and paper making became mechanised in the 19th century, along with the development of the printing press, alternative fibre sources were required to meet the higher demand. Wood fibre, being plentiful, was introduced<sup>17,18</sup>, and when it was bleached formed an adequately aesthetic paper sheet.

Wood, however, undergoes rapid light-induced discolouration. The main difference between wood and the earlier, more light-stable fibre sources is the impurity of the cellulose fibre. Cellulose is a white polysaccharide consisting of a large number of anhydroglucose units<sup>17,19</sup>. Although it has been shown to undergo photo-degradation upon irradiation with low UV light (253.7nm), terrestrial sunlight contains wavelengths above this level (>300nm) and thus has little effect on cellulose<sup>19,20,21</sup>. In fact, early fibre sources with high cellulose purity such as rag and cotton were actually bleached using sunlight. As a result of this good photostability or permanence of pure cellulose (and other factors, including durability, uniformity of web, colour, texture and surface, and superb writing and erasure properties) 100% rag paper is still used for the manufacture of paper required for permanent records (for example, banknotes and other securities, technical papers, legal documents, specialist letterheads, light-weight specialties, high-quality writing, and some conservation applications)<sup>17</sup>.

The inability of rag pulp manufacturers to meet the demand, however, as well as the overwhelming popularity of wood pulp (for economic reasons) has resulted in most papers being composed predominantly or entirely of wood pulp<sup>17</sup>. Wood fibres also

consist of cellulose, but have a large amount of other components which vary in proportion depending on the type of tree, its age and other factors which are not completely understood. In general, however, the composition of wood is 40-50% cellulose, with other components including 20-30% lignin, 15-25% hemicelluloses, and 5-10% composition of waxes, fats, oils, tannins, resins and gums<sup>17</sup>. Hemicelluloses are polysaccharides, but unlike cellulose consist of several different types of sugar units (for example mannose and galactose) in the one chain. Lignin, on the other hand, is a non-polysaccharide random polymer. The greatest concentration of lignin is found in the middle lamella, but most lignin is located in the secondary wall, albeit in low concentration. Being infused throughout the fibre, it is an important binding agent within the fibre<sup>17</sup>. Although its complete structure is not yet known for certain (see Section 1.2), it is known that lignin contains chromophoric groups which absorb higher wavelength UV light well within the region of terrestrial sunlight, turning a brownish-yellow colour. This light-induced discolouration of lignin is the main cause of yellowing of wood-derived pulps and papers on exposure to sunlight.

### **1.1.3 Is it a problem in all pulps and papers derived from wood?**

No. The problem of photo-induced reversion of wood-derived pulps and papers was resolved, to a certain extent, with the development of chemical pulping. This involves the use of chemical processes that delignify (remove the lignin component of) the fibre, thus leaving a relatively photo-stable pulp consisting mainly of cellulose. To remove lignin, however, is to remove a large portion of this fibre source. Naturally this creates a low-yield pulp, with about half of the woody material being removed<sup>22</sup>. Thus low-life papers which do not require a long-term stability, such as newsprint, are made from pulp that has not undergone delignification treatments. These pulps are referred to as high-yield pulps, as the retention of the lignin components allow a yield which can approach 100%<sup>1b</sup>, about twice that of chemical pulp. Of course, these pulps do undergo rapid reversion when exposed to sunlight, and this is the major factor limiting their use in more permanent papers such as printing papers<sup>13,23,24,25,26</sup>.

### **1.1.4 Why should we try to prevent light-induced reversion of high-yield pulps?**

The driving force in trying to prevent light-induced reversion of high-yield pulps is the desire to use them in higher grades of paper, thus increasing their market and at the same time replacing at least some of the chemical pulps already used in higher grade papers. In order to justify such a motive, it is necessary to discuss the



advantages and disadvantages of these two types of pulp. It would be easy to digress into a large review of the different types of chemical pulps and high-yield pulps, their histories, manufacturing processes, advantages, disadvantages and so forth. There is an abundance of literature available on this topic, however, including several books (for example Casey<sup>16</sup>, R.P. Singh<sup>1</sup>, C.E. Brandon<sup>20</sup> and so on). Instead, the main comparative advantages and disadvantages for chemical and mechanical pulps will be discussed. It should firstly be noted, however, that there are several kinds of chemical (e.g. Kraft pulp) and high-yield pulps (e.g. groundwood (GW) and thermomechanical pulp (TMP)). Although each individual pulp has its own unique properties, the main differences in the properties between the two classes of pulp (i.e. between chemical and high-yield pulps) are universal and outweigh the smaller differences observed between pulps belonging to the same class.

Arguments against replacing chemical pulp with high-yield, or mechanical pulp in higher grade papers pertain mostly to the superior light stability and strength of chemical pulp over mechanical pulp, along with the high cost of electrical energy needed to manufacture TMP. Arguments favouring the replacement of chemical pulp by TMP are based mainly on the environmental impact of the chemicals related to chemical pulping along with its low yield and therefore inefficient usage of forest resources. Each of these arguments are presented below, along with a prediction of their importance in the future.

Before continuing, a third class of pulp should also be introduced, which is manufactured by a combination of the above two processes, thereby exhibiting a combination of both chemical and mechanical pulp properties. These are the chemithermomechanical (CTMP) or chemimechanical pulps (CMP), which have undergone chemical pre-treatment to loosen their fibres while removing only a partial amount of lignin. These pulps thus have higher strength than mechanical pulp, approaching that of chemical pulp, but due to their lignin content still undergo rapid photo-induced reversion approaching that of mechanical pulp.

### ***Arguments for the replacement of chemical pulps, or at least inclusion of high-yield pulps in the manufacture of higher grade papers***

#### ***Environmental concern, impact of chemicals***

The damaging impact on the environment from chemical pulping has been one of the major arguments for the replacement of chemical pulps with mechanical pulps in the past. For elemental chlorine-bleached pulp in particular, the production of toxic dioxin by-products from the reaction of chlorine with lignin along with the production of other chlorinated organic compounds has been of major concern, with

governmental limitations already existing in some countries which hinder the use of this process.

Recent progress in the chemical pulp industry, however, has rendered such an argument redundant. Novel ways have already been found to continue the use of chlorine compounds without the production of chlorinated dioxins and furans<sup>22</sup>, including replacement with chlorine dioxide ( $\text{ClO}_2$ )<sup>27</sup> or Monox-L (a bleaching agent that contains both hypochlorous acid ( $\text{HOCl}$ ) and a nitrogen compound)<sup>28</sup>. A number of chlorine-using mills today have already replaced elemental chlorine with chlorine dioxide<sup>27</sup> (referred to as ECF or elemental chlorine free bleaching).

Some concerns still exist, however, as this is still a chlorine compound and although harmful by-products from its usage have not been established, chlorine certainly has developed a stigma about it and many people want to phase its use out entirely. One such person is the environmentalist Joe Thornton (research coordinator for Greenpeace's International Chlorine-free Campaign) and statistics presented by him in 1995 revealed the pulp and paper industry to contribute 15% of the 40 million tons of chlorine produced annually by the chemical industry (as cited by P. Pauksta, *Tappi Journal*, 74(4), 1995<sup>27</sup>). This argument is also being reduced, however, as research is being carried out into more bleaching processes that are totally chlorine-free (TCF). Examples of such processes include oxygen delignification/bleaching<sup>29</sup>, ozone bleaching<sup>30</sup>, hydrogen peroxide bleaching<sup>30†</sup>, UV bleaching<sup>31</sup> and even bleaching using enzymes<sup>30</sup> and fungi<sup>32</sup>. In fact, oxygen delignification is already a widespread practice in the paper mill, and along with the introduction of new methods and equipment such as displacement bleaching a considerable effort has indeed been made to reduce the pollution from bleach plant effluents<sup>29</sup>.

There have also been many discussions on the future of Kraft mills, with indications that there will indeed be success in minimising environmental concerns in the future<sup>33,34,35</sup>.

It would seem, therefore, that with all the progress in chemical pulping it is certainly only a matter of time before the environmental impact *with respect to* chemical contamination will not be a compelling argument for its replacement by mechanical pulp.

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<sup>†</sup>It should be noted that the hydrogen peroxide bleaching conditions are different for chemical pulp and mechanical pulp and the processes should not be confused. Chemical pulp reaction conditions are such that hydrogen peroxide has delignifying properties, but for mechanical pulp the milder conditions encourage peroxide reactions which bleach chromophoric groups without removing lignin.

### *Low yield of chemical pulp*

Low yield has been a second argument for the replacement of chemical pulps by mechanical pulps. Despite all the improvements being made in chemical pulping, the mere fact that lignin is being removed means that yield will never be able to match that of mechanical pulp, or even come close. To make a given tonnage, twice as many trees need to be cut down for the manufacture of chemical pulp compared with that of mechanical pulp<sup>36</sup>. Even modest levels of delignification (e.g. 30%) have little effect on improving yield<sup>37</sup>.

Thus, considering the improvements being made in the environmental impact of chemical pulping, the argument for replacing chemical pulp with mechanical pulp may become predominately a question of yield. This by itself is a compelling argument. With concern for natural forests and continuing governmental restrictions, it certainly makes sense to maximise the usage of these resources. As it takes twice as many trees to make the same quantity of chemical pulp as it does to make mechanical pulp, then bringing mechanical pulp standards up to chemical pulp standards with a view to replacing chemical pulp is certainly a worthwhile goal.

### *Arguments against the inclusion of high-yield pulps in the manufacture of higher grade papers*

#### *Inferior strength of TMP*

One disadvantage of high-yield or mechanical pulp lies with its inferior strength properties compared with those of chemical pulp. Studies on the mechanical properties of papers containing mixtures of chemithermomechanical pulp and chemical pulp by Priest and Stanley<sup>38</sup>, however showed that the CTMP containing papers were able to retain their strength properties on aging just as well as wood-free grades. So although the original strength of CTMP was slightly less than chemical pulp, the incorporation of CTMP had a negligible effect on the rates of strength loss. Improvements in refining technology have also increased high-yield pulps' strength sufficiently that mechanical pulps could theoretically replace some of the chemical pulp component in higher value furnishes<sup>24</sup>. An article written by Derek Page<sup>39</sup> discussing the current national and international standards for permanent papers (that the lignin content must be less than 1%) concurs that there is a lot of good scientific evidence that lignin has no effect on mechanical (or strength) permanence. He believes that these restrictions are unnecessary and would not need to exclude several high-yield pulps (for example stone-ground wood (SGW), TMP and CTMP) from

use in permanent papers. So the inferior strength of TMP to chemical pulp is not a significant argument for the exclusion of TMP from high grade paper manufacture.

#### *High electrical energy requirement for TMP*

Another disadvantage of mechanical pulping is the high amount of relatively expensive electrical energy required for its production, but research is also currently underway to reduce this energy requirement. An article by Bolker<sup>36</sup> describes a large collaboration of researchers (called The Mechanical and Chemimechanical Pulps Network, Canada) working on several aspects of mechanical pulping. Included in his report were the results of pilot-plant trials using modified disc-refining techniques, carried out by Stationwala and coworkers of Paprican (Pulp and Paper Research Institute of Canada). They were able to produce a black spruce pulp with properties equivalent to those of a conventionally produced pulp while using less than 75% of the total applied energy. Another article by Meadows<sup>40</sup>, also discussing current trends in mechanical pulping research, reported that the recent introduction of a new TMP process resulted in reductions in specific energy requirements from 2000-2200kW·h/ton to about 1300-1400kW·h/ton. Predictions cited in the article by Meadows anticipate this to be reduced even further to below 1000kW·h/ton by the year 2005. Thus it is possible that mechanical pulping may become more cost-efficient in the future, and its high electrical energy requirement may become less significant in arguing against its inclusion in higher-grade papers.

#### *Light-induced colour reversion of high-yield pulps*

A third argument against the use of high-yield pulps in high-grade papers is the tendency of such pulps to readily undergo light-induced reversion. This is one area that has yet to be resolved. Light-induced reversion of high-yield pulps is, in fact, the main factor in their exclusion from higher grade pulps and papers. While photo-reversion of paper containing mechanical pulp or ultra-high yield pulp can cause a reduction in brightness of more than 30 ISO units in a short time, a drop of only approximately 3 units is observed for Kraft chemical pulp under identical conditions<sup>41</sup>. Despite an abundance of research having been done on this problem, a cost efficient and effective reversion inhibition method for high-yield pulps has yet to be achieved. One problem in reaching this goal has been that the full process of this form of reversion has not yet been elucidated, although many reaction pathways have already been deduced. As a result of the dedication applied by many researchers in this area a substantial amount of information has been uncovered about both the reactions and species involved in light-induced reversion reactions,

and possible ways in which to inhibit them. These are discussed in detail in the following two sections (Sections 1.2 and 1.3).

Thus it appears that of the main disadvantages of the inclusion of TMP in higher grade papers, light-induced reversion remains the only real problem. The small loss in strength occasioned by using these fibres is a small price to pay, and there is comfort in knowing that a further loss in strength will be minimal. The energy requirements will also be minimised in the future.

#### **1.1.5 Predictions for the future of the TMP industry if light-induced reversion can be prevented or at least minimised**

As previously mentioned, light-induced reversion of mechanical pulp is the major factor preventing it from replacing chemical pulps and being used more extensively in the paper industry. If this reversion can be stopped or at least minimised then TMP (or at least CTMP), currently used for the manufacture of short-life papers (such as newsprint and advertising inserts, directory paper and some catalogue papers), could also be used in furnishes for the manufacture of long-life or higher value grades of paper, including business forms, copy and reprographic papers, tablet and writing papers, and even high-grade publication papers for books<sup>36,41</sup>. In 1989 a presentation by Cockram<sup>42</sup> discussed the findings from interviews with over 400 specifiers of wood-free papers from several countries. Included was a survey of North American printers and publishers with findings that two thirds of them would use paper containing bleached CTMP if the paper was stable to light for one year<sup>43</sup>. From these findings Cockram predicted that if the life of CTMP could be increased to only 3 months its usage could be increased by 1.4 million tonnes per year. If the life could be sustained indefinitely such that brightness instability was not a factor, then the use of these pulps could be increased even more, by 7.1 million tonnes per year<sup>42</sup>. CTMP would thus represent more than 40% of the total printing and writing market<sup>26</sup>. An article by Nissan<sup>22</sup> suggests that if a "90-90-9" pulp (90% yield, 90% brightness and 9km breaking length) could be made with a non-reverting brightness, it would double the yield of the forest in terms of tons of bright, strong pulp per acre when compared to current chemical pulps. Basically if light-induced reversion of high-yield pulps could be arrested or minimised the market for these pulps would increase dramatically, along with the efficiency of utilisation of forest resources by the pulp and paper industry.

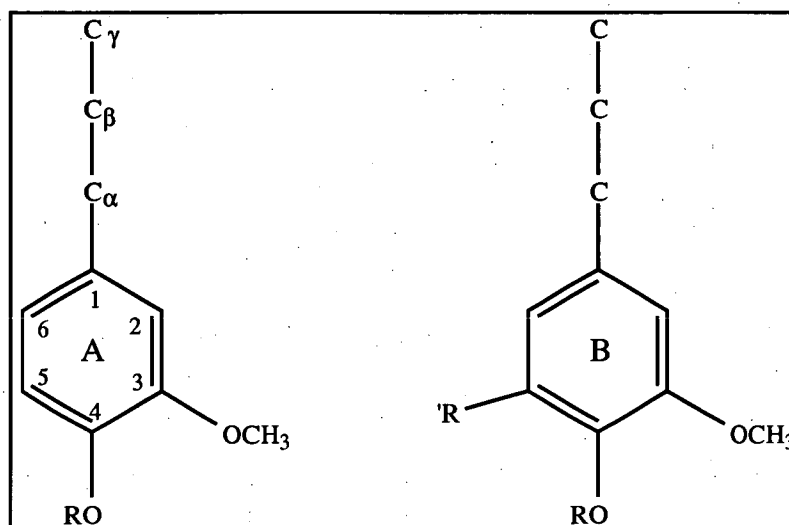
## **1.2 An Historical Review of the Development of Our Understanding of the Structure of Lignin and Reaction Mechanisms for its Light-Induced Discolouration**

Proposed structures have been suggested for lignin throughout the history of lignin chemistry, but a complete understanding has yet to be reached. Much research has been undertaken in an attempt to define processes occurring during its photo-discolouration, and again a complete answer has eluded researchers, as the lignin macromolecule is very complex. The process has been made simpler however, through the use of model lignin compounds (MLCs) to simulate lignin reactive groups. Such compounds are generally suspected to be contained within the lignin moiety, and their reactions are assumed to give a representation of the chemical processes occurring. Of course, without the steric hindrances and interfering forces (e.g. H-bonding, various dipole influences etc.) coming from the rest of the vast lignin molecule, lignin model compounds can never give the complete story, but they are a good starting point. As the understanding of lignin's structure has changed through time, so too have the MLCs being studied. The following pages are intended to give a brief history of early lignin chemistry, up to the present state of knowledge. Construction of proposed lignin structures, and the functional groups they contain will be discussed, but the main focus will be on the mechanisms and components involved in light-induced discolouration reactions. The literature to be discussed include findings based on both "lignin" (i.e. lignin in its native form contained within wood or pulp, or lignin isolated by chemical extraction of its native form) and / or MLCs.

Most of the groundwork on lignin chemistry was established in the 1970s, but significant contributions began 2-3 decades before this. Prior to 1970, it had been established that lignin was the primary cause of photo-yellowing in both wood and high-yield pulps. It was generally accepted that oxygen played an essential role, suggesting that photochemical oxidation was the major reaction involved during exposure of lignin to light<sup>7,18,44,45</sup>. The mechanisms involved, however, were a mystery, and the structure of lignin was unknown. To understand what was happening, two concurrent lines of investigation began to flourish - an attempt to determine the structure or at least structural components of lignin, and an attempt to understand the chemical processes involved in photo-yellowing. The existence of many methoxyl and hydroxyl groups in lignin became well known, their proportions varying depending on the lignin type and its treatment.

Conjectured specific lignin constituents included quinones<sup>44,46,47</sup>, hydroxyl phenylketones, *p*-quinone methides, and carbonium ions contained within a carbohydrate and phenylpropane macromolecular system<sup>46</sup>. Also suggested were *p*-

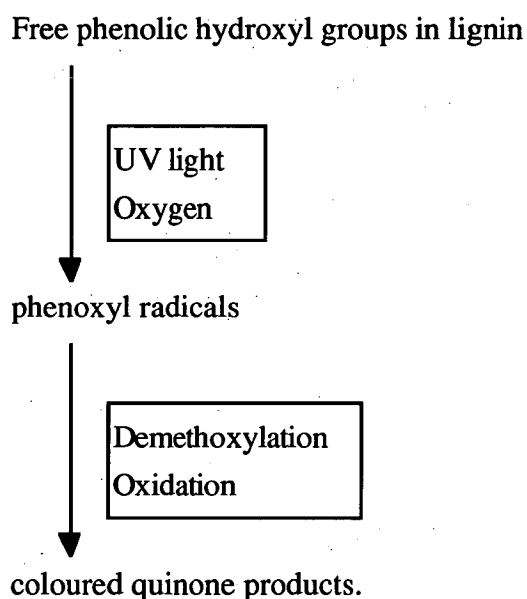
substituted-*o*-methoxyphenoxy, *p*-substituted-*o-o'*-dimethoxyphenoxy and *p*-substituted phenoxy groups, along with quinone-hydroxybenzene systems,  $\alpha$ -diketone and polyene structures<sup>47</sup>. Freudenberg (as cited by Adler and Lundquist<sup>48</sup>) introduced the proposal that lignin contained two general types of arylpropane units, characterised as either “uncondensed” or “condensed” (Figure 1.1).



**Figure 1.1.** Two basic arylpropane units in lignin. A = “uncondensed”, B = “condensed”, where R = H or C and ‘R = C of an aromatic ring or side chain of an adjacent arylpropane unit (adapted from E. Adler and K. Lundquist, *Acta. Chem. Scand.*, 15 (1), 1961<sup>48</sup>).

The uncondensed units contained an unsubstituted carbon in the 5 position, while the condensed version contained a substituted carbon in this position. Both types contained either a free or etherified phenolic hydroxyl group. It was this proposal upon which Adler and Lundquist based several oxidation reactions (using Fremy’s salt), using model compounds derived from these structures<sup>48</sup>. They found that compounds of the condensed version did not oxidise. The uncondensed version containing a free phenolic hydroxyl group, however, oxidised to form *o*-quinone structures which were red in colour and produced characteristic absorption spectra. (It should be noted that Adler and Lundquist also discovered the same type of uncondensed unit oxidised to give a *p*-quinone when H and OH were substituted on the  $\alpha$ -C, while no oxidation occurred when the  $\alpha$ -C contained a keto group). When oxidising a pre-treated lignin sample, they also discovered a red colouration along with a similar absorption spectra to that obtained above. Therefore they established that *o*-quinones were a major product of lignin oxidation. Many other authors also concurred with this finding, that quinones<sup>7,44,47,49,50,51</sup>, quinone methides or cyclohexadienones<sup>45</sup> were most likely to be the main product of oxidation and / or photo-induced oxidation of lignin.

Other products of oxidation or irradiation of lignin were also identified, such as vanillin<sup>4,7,18,48</sup>, syringaldehyde, CO<sub>2</sub>, CO, H<sub>2</sub>O, methanol<sup>7</sup>, vanillic acid and a few sugars<sup>4</sup>, but most work centred about deducing a reaction mechanism for production of the quinones. It was generally agreed upon that the source of these quinones was the free phenolic hydroxyl groups<sup>7,44,47,48,49,51</sup>, as irradiations performed after effectively “blocking” or removing these groups exhibited a lesser yellowing<sup>45</sup>. Leary proposed a mechanism which involved abstraction of phenolic H from a neighbouring excited molecule or free radical. It was observed that during irradiation a significant loss of methoxyl groups occurred<sup>4,7,44</sup>, and free radicals were produced<sup>7</sup>. Thus the 1960s ended with the proposal that photo-yellowing of lignin involved the following reaction mechanism:



The 1970s saw an “explosion” of further knowledge of lignin chemistry, both in its structural determination and in reactions involved during light-induced reversion. Lignin chemistry began to lose its simplicity, becoming an extremely complicated field. As more became known of its structural components, further proposals for lignin structures were made, each one becoming more complex. For example, from results of many reactions involving beech lignin, Nimz<sup>52</sup> presented a proposal in 1973. This scheme contained no less than 25 phenylpropane units containing various side groups and linkages. In all the structural scheme gave the molecular formula C<sub>259</sub>H<sub>281</sub>O<sub>95</sub>. Casey<sup>16b</sup> took structural analysis of lignin further, citing a structure proposed by Glasser & Glasser. This structure contained 81 phenylpropane units, with a molecular weight of about 15,000. In 1977 Adler<sup>53</sup> presented a simpler version of softwood lignin containing 16 phenylpropane units. Each structure appeared to be scientifically sound and many similarities can be seen in each. The first two mentioned, however, are very complex and it is beyond the scope of this thesis to reproduce them. (The interested reader is encouraged to consult the original



references). Adler's version has been reproduced in Figure 1.2, so one can see the main structural components and linkages of the lignin macromolecule. (It should be noted that most, if not all, groups mentioned in Alder's scheme are also common in the above two schemes, although the proportions vary. This is due to the different lignin types studied. For the purpose of this thesis, only a general structure of lignin is warranted, while keeping in mind that proportions of components and existence of minor components may vary with each lignin type.)

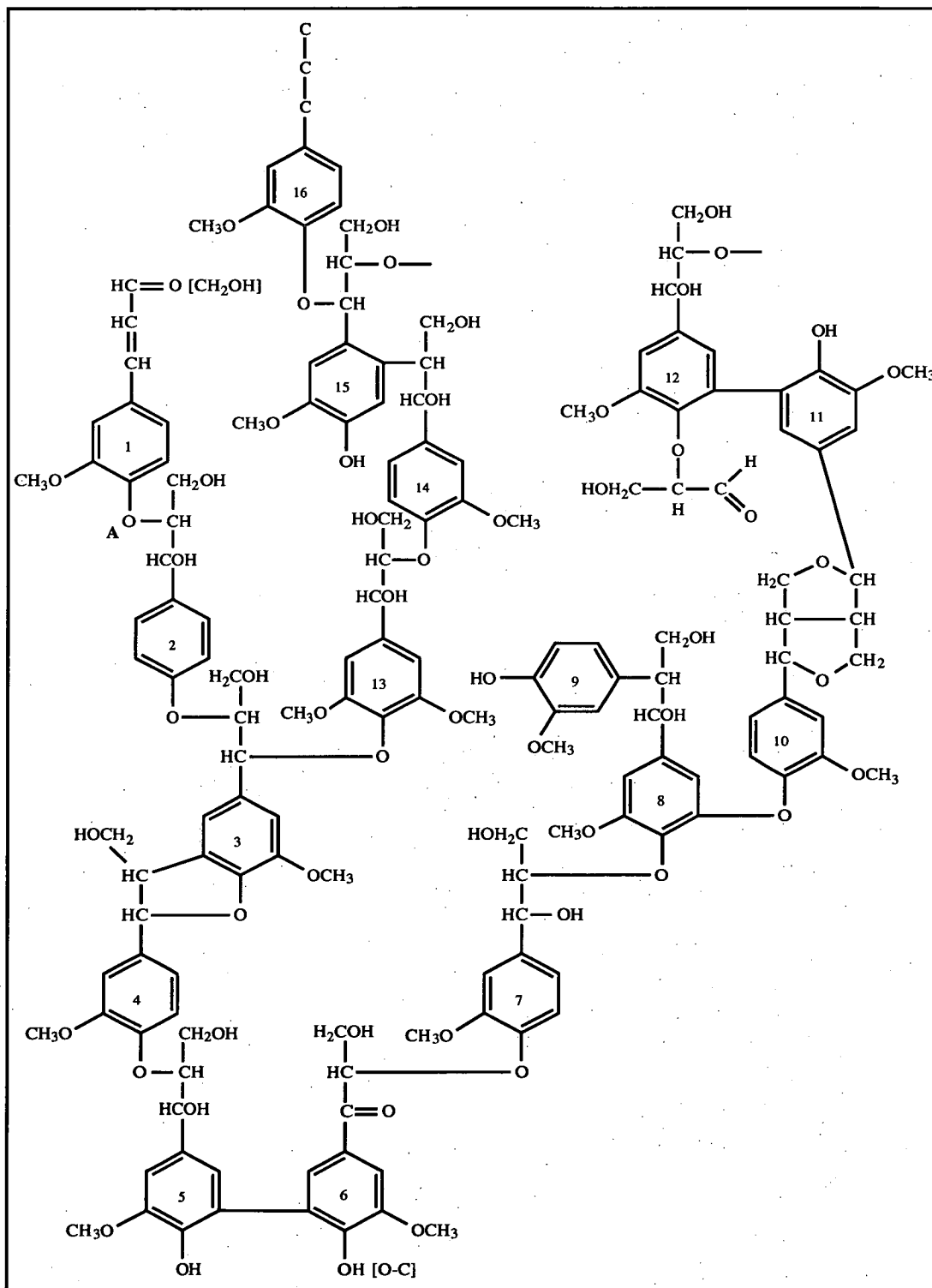


Figure 1.2. Simplified model of the structure of lignin<sup>53</sup>.

Looking at Figure 1.2, the abundance of ether linkages is clear. These are of several types, but are predominantly of arylglycerol- $\beta$ -aryl ether type (A). A summary of each linkage type, along with their structures can be seen in the reference. Common components in the lignin macromolecule include several methoxyl groups, phenolic and non-phenolic hydroxyl groups, and many 3-carbon side chains. Various moieties are present, including hydroxyl groups, aldehyde and keto groups, carboxyl groups and C=C double bonds in the arylpropyl side chains.

As the importance of high-yield pulps grew in the 1970s, so too did an awareness of the problems of photo-induced yellowing. Thus much research was done into trying to understand mechanisms for this process. Many authors based their research on the previously established involvement of phenoxyl radicals. "Old" methods of analysis were used, along with a growing number of new techniques, including the use of model lignin compounds, selective oxidation and reduction reactions, UV-visible absorption difference spectroscopy, selective blocking or removal of specific functional groups, electron spin spectroscopy (ESR), gas chromatography (GC), mass spectroscopy (MS), and others. By various means three significant elements in the yellowing process were discovered, with general agreement. These were as follows:

1. Phenoxyl radicals were indeed the precursors to yellow product formation, possibly via reaction with oxygen<sup>54,55</sup>.

2. Alpha-carbonyl groups were fundamental to the yellowing process<sup>56</sup>, although they did not react to form yellow products themselves, and were recoverable post-reaction, in their original state. It was concluded that these species aided photo-reaction indirectly, i.e. they behaved as photo-sensitisers<sup>57,58</sup>.

3. It was unclear whether the excited carbonyl group exerted its action directly or indirectly. In the case of a direct mechanism, it has been suggested that the excited conjugated  $\alpha$ -carbonyl groups were able to abstract a H from phenolic hydroxyl units, thus generating the phenoxyl radicals<sup>55,57</sup>. Some authors saw a problem with this theory. It was thought unlikely that the carbonyl group would have the required mobility within a solid (paper or wood) matrix to sensitise sufficient phenolic hydroxyls to induce yellowing to the extent observed. The indirect mechanism was therefore proposed. This mechanism involved the excited carbonyl group transferring its energy to a very mobile oxygen molecule, inducing a highly energetic oxygen singlet. This oxygen singlet could then abstract H from phenolic hydroxyls. Thus it was proposed that oxygen actually becomes involved in the reaction, as a kind of energy transfer agent.<sup>54,58</sup> Considering the mobility factor compared to the extent of yellowing observed, the latter reaction seemed more

favourable. However, it is likely that the two mechanisms occur simultaneously and yet at differing rates.

Other reasonable reaction schemes were suggested (for example see Gierer & Lin<sup>59</sup>), along with other chromogenic groups or possible sensitisers such as C=C bonds and biphenyl structures<sup>55</sup>. However, these did not simulate the response to light of native lignin as well as the  $\alpha$ -carbonyl group discussed above<sup>56</sup>. Basic similarities exist between Gierer and Lin's proposals and the discussed proposal above. These include the role of sensitising groups, and fundamental hydrogen abstraction steps, particularly on the phenolic hydroxyl group. The main difference in Gierer & Lin's proposals<sup>59</sup>, is they suggest the formation and involvement of hydrogen radicals and oxygen to create hydroperoxyl radicals, which abstract hydrogen. They also introduce the possibility of a "cycling" of radical groups, setting up some kind of radical-involved chain reaction.

Lignin chemistry with respect to structural components and yellowing mechanisms slowed down during the 1980s, when the focus shifted towards other areas of paper science, particularly the mechanisms of hydrogen peroxide bleaching. Glasser & Glasser<sup>60</sup> investigated the structure of lignin further, creating a model with 94 phenylpropane units. Their findings revealed little new information about the structure, but in the course of their work they developed a more improved computer simulation technique for its elucidation.

On the photo-chemistry of lignin, Lebo et al.<sup>61</sup> developed a new method for determining the occurrence and amount of *o*-quinoid structures in pulp. They were able to show that these structures were originally present in pulp, and their amount was vastly increased during exposure to simulated sunlight. This was an important discovery, as *o*-quinones had long been suspected to be the main yellowing product (as discussed above, Adler & Lundquist<sup>48</sup>). Evidence for this, however, had been quite circumstantial as they were based mainly on results of Fremy's salt oxidation experiments, and relied on the assumption that the photo-chemical and oxidation reactions were similar. Schmidt et al.<sup>62</sup> also introduced a new technique for lignin analysis. They used diffuse-reflectance laser-flash photolysis to identify the transient species in the light-induced yellowing of TMP. This was found to be the lowest energy triplet excited state of the carbonyl chromophore in lignin. Their findings support the reaction mechanism above, involving the carbonyl group as the main sensitiser. Schmidt et al. believed, however, that singlet oxygen didn't play as large a role as previously suspected, citing findings by Forsskåhl et al. (referenced therein) which showed that singlet oxygen in the absence of light induced no discolouration. They did suggest that the triplet carbonyl abstracted a H directly, (as suggested in the

1970's scheme above), from neighbouring phenolic hydroxyl groups ("static abstraction"). To substantiate the amount of yellowing observed in a solid matrix, they suggested that dynamic abstraction also occurred by excited carbonyl triplets which were not within range of phenolic hydroxyls, through alternative pathways which also lead to yellow products. What these alternative pathways could be was not yet known, but suggestions indicated the possible involvement of alcoholic benzyl groups and others.

Forsskåhl et al.<sup>63</sup> initiated studies on methoxy-*p*-benzoquinone, another species suggested to be an intermediate in the photo-yellowing processes. They found that this species underwent dimerisation upon irradiation, producing strongly coloured products. Tatsumi<sup>63a</sup> also found photo-induced oxidative coupling reactions to occur during UV irradiation of vanillic acid.

The 1990s saw scientists researching the above mechanisms and new ones fervently. Environmental concerns had become paramount, and results that would give an insight into photo-yellowing became essential to enable more research into inhibiting these photo-yellowing reactions. New experimental procedures were employed (Fourier transform infra-red spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), and others), along with a wider range of MLCs. Most research focused on the formation of the phenoxyl radical, generally accepting that the final steps of discolouration were similar, i.e. constituted by the oxidation of phenoxyl radicals to coloured quinones.

Naturally with so much research being done, contradictions began to emerge in many aspects of the photo-discolouration pathways. For example - the role of singlet oxygen - did it have a role after all? Forsskåhl et al. had already expressed doubts in the previous decade. In support of singlet oxygen, Beyer et al.<sup>64</sup> suggested that singlet oxygen had a significant role in light-induced homolytic cleavage of lignin polymer chains, and Wang et al.<sup>65</sup> suggested singlet oxygen formed oxygen based free radicals that can abstract a benzylic H, with subsequent formation of the phenolic groups. But results of an initial investigation by Agnemo et al., (cited in a later paper<sup>66</sup>), indicated the unlikelihood of singlet oxygen to have any significant role in photo-yellowing. However, they did support the proposal that the formation of phenoxyl radicals occurred via an abstraction of the phenolic H by a photo-excited ring-conjugated carbonyl group, or by a hydroxyl radical formed from the photolysis of hydrogen peroxide or hydroperoxides, which had themselves been formed by oxygen-sensitiser charge transfer complexes. The work done by Agnemo et al. revealed that hydroxyl radicals were indeed generated and did play an important role in the overall yellowing process. Fornier de Violet et al.<sup>67</sup>, on the other hand,

suggested a direct photolysis of phenolic and  $\alpha$ -carbonyl structures to produce phenoxyl radicals. Schmidt & Heitner<sup>68</sup> showed the formation of aromatic ketones and quinones when irradiating peroxide bleached thermomechanical pulp (BTMP). This contradicted previous proposals that aromatic ketones acted as sensitisers in photo-yellowing, because if they did, they would not appear as a reaction product. Schmidt & Heitner also found that phenolic hydroxyl groups have only a small contribution to the yellowing process. It is likely, however that peroxide bleached TMP, lacking at least one source of aromatic ketones in the form of  $\alpha$ -coniferaldehydes (as peroxide bleaching effectively removes these structures), undergoes a different reaction pathway to unbleached TMP.

More components of lignin were discovered. Also some "lignin reaction products" were found to either already exist in small amounts in natural lignin, or were introduced during mechanical pulping and/or peroxide bleaching. Some of these structures were also suspected to play a role in the discolouration process. For example, stilbenes were shown to be formed partly during grinding or disc refining of pulps, and largely during peroxide bleaching<sup>69,70</sup>. These stilbene structures were shown to enhance the discolouration by light (especially for the presence of diguaiacyl stilbene structures in peroxide bleached pulps, which underwent severe yellowing that could not be ascribed solely to coniferaldehyde structures implicated in previous schemes). It has been suggested that the yellowing reactions resulting from stilbene structures involved abstraction of a H from ground state stilbene by an excited stilbene molecule or an oxygen molecule in an excited complex. From this, stilbene phenoxyl radicals were formed. These oxidatively lost an electron to another phenoxyl radical, hydroperoxide radical or oxygen, forming a stilbene cation, which subsequently reacted to form *o*-quinone structures. Other photo-reactions also occurred, including cyclodimerisation, cleavage and oxygenation of the stilbene double bond, but not all of them produced yellow products<sup>70</sup>.

Several quinonoid structures were also shown to form during mechanical pulping processes<sup>71</sup> and/or peroxide bleaching<sup>72</sup>. Much work has been done on these quinone structures, mainly through MLC studies, and they have been shown to significantly contribute to photo-yellowing<sup>71,72,73,74</sup>, with both *ortho*- and *para*-quinones causing discolouration. Some pathways thought to have occurred include dimerisation of quinoid monomers (e.g. methoxy-*p*-benzoquinone), followed by cyclisation to form a dibenzofuran-1,4-quinone derivative, which even at low concentrations made pulp visibly yellow<sup>72</sup>. Different lignins contain different quinone types and different relative concentrations of each quinone type, so some reactions involving quinones would be more predominant for different lignin types<sup>74</sup>.

Agarwal & Atalla<sup>75</sup> found coniferyl alcohol structures to also be present in peroxide bleached TMP, and proposed that they too were precursors of yellowed irradiation products.

One of the most recently accepted reversion mechanisms, and indeed one of the most studied, is the breakdown of the arylglycerol- $\beta$ -arylether linkage. It has recently been found to be a major source of coloured groups in photo-yellowing of mechanical pulps<sup>76</sup>. Several authors found evidence (through irradiation of lignin) of cleavage of  $\beta$ -O-4 inter-unit bonds<sup>12,77</sup>. (Also found was a decrease in  $\beta$ -1 inter-unit bonds<sup>77</sup>, a higher condensation degree<sup>77</sup>, an increase in catechol units<sup>77</sup>, vanillin end groups<sup>12,77,78</sup> and the formation of vanillic acid<sup>12,78</sup>). Degradation of the arylglycerol- $\beta$ -arylether group is thought to occur via corresponding ketyl radicals (formed by H abstraction by a triplet excited carbonyl group<sup>79,80</sup>), which cleave the  $\beta$ -O-4 bond rapidly, to give a phenoxyl radical and an acetophenone enol<sup>80</sup>. The enol tautomerises to a ketone, while the phenoxyl radical oxidises to form coloured groups<sup>76,81</sup>. Heitner<sup>82</sup> suggested an alternative pathway, in which the  $\beta$ -O-4-aryl ether cleavage occurs via light-induced peroxy and alkoxy free radicals. The increase in vanillin and vanillic acid end groups is thought to result from oxidative cleavage of  $C_{\alpha}=C_{\beta}$  bonds<sup>77</sup>. Sjöholm et al.<sup>78</sup> have taken the analysis of the whole process a little further, identifying many more products, including an  $\alpha$ -ether bond cleavage; an increase in terminal groups containing aromatic aldehyde and carboxyl groups; transformation of existing  $\alpha$ -carbonyl groups to carboxyl groups; generation of new  $\alpha$ -carbonyls, possibly from -CHOH groups; a decrease in methoxyl content; some degradation of aromatic rings and degradation of phenylcoumaran units. They proposed that stilbenes and stilbene derived chromophores could also be formed from  $\alpha$ -ether cleavage of the phenylcoumarans. Interestingly they observed no formation of quinones, but suggest they could still have been present as reactive intermediates in the process.

## Summary

Currently there are many different views on the mechanisms of photo-discolouration. It is difficult to assess which ones are accurate and which ones are not, as each contradiction to a particular mechanism may be explained simply by the different model compounds or lignin types studied exhibiting different pathways. It is possible that each proposed pathway is an accurate assessment, occurring to varying degrees or not at all, depending on the type of lignin and any treatments it has been subjected to. Until more is known about each type of lignin, and the changes

occurring in it produced by pulping, bleaching, sheet formation (heating), it is safest to consider each proposed mechanism as a possibility, while also realising that many more pathways are also likely to be present. Considering the speed in which research into this field is progressing, many new reaction pathways will have been proposed within the next few years. For the present though there appears to be four general steps in the photo-yellowing pathways, which are as follows:

### ***Step 1. UV absorption***

This is generally accepted to occur by an alpha-carbonyl group absorbing UV radiation and being transformed into an excited state. Other UV absorbing groups could include C=C bonds, etc. These excited groups could then initiate Step 2 either directly, or indirectly by transferring their energy to other groups like oxygen to form excited singlet states which can then initiate Step 2. Alternatively UV absorption and oxygen involved processes could lead to the formation of simple radical species like hydroperoxide radicals, hydroxyl radicals, peroxy radicals etc., which can then initiate Step 2.

### ***Step 2. Formation of radical intermediates***

This is generally accepted as occurring via H-abstraction from a free phenoxy hydroxyl group to form a phenoxyl radical. This abstraction is by an excited group or simple radical from Step 1. Other groups, for example benzylic groups, can also form radical intermediates via H-abstraction. Alternatively radicals can be formed via cleavage of bonds, like the  $\beta$ -O-4 bonds.

### ***Step 3. Formation of yellow products***

The phenoxyl radicals formed in Step 2 can be oxidised and demethoxylated to form quinones. Alternatively, other radicals formed in Step 2 can oxidise to produce other coloured species. The radicals could also undergo dimerisation with other radicals or cyclisation to form other yellow products.

### ***Step 4. Establishment of chain reactions***

Finally, the radicals formed in Step 2 could also react with lignin groups, forming other radicals which could then either undergo Step 3, or feed back into a "radical cycle" and further propagations of yellowing reactions.

### 1.3 Inhibiting the Photo-Induced Reversion of Lignin-Rich Pulp and Paper

The previous section outlined proposed yellowing mechanisms, and it is on the basis of these pathways that most inhibition methods are considered. Figure 1.3 is a schematic reproduction of the summary of yellowing mechanisms proposed in the previous section, with indications of theoretically possible inhibition target areas. As can be seen from this figure, there are several avenues to explore, each with advantages and limitations. This section will discuss several approaches which have been or are being explored in employing each of these possible methods of inhibition.

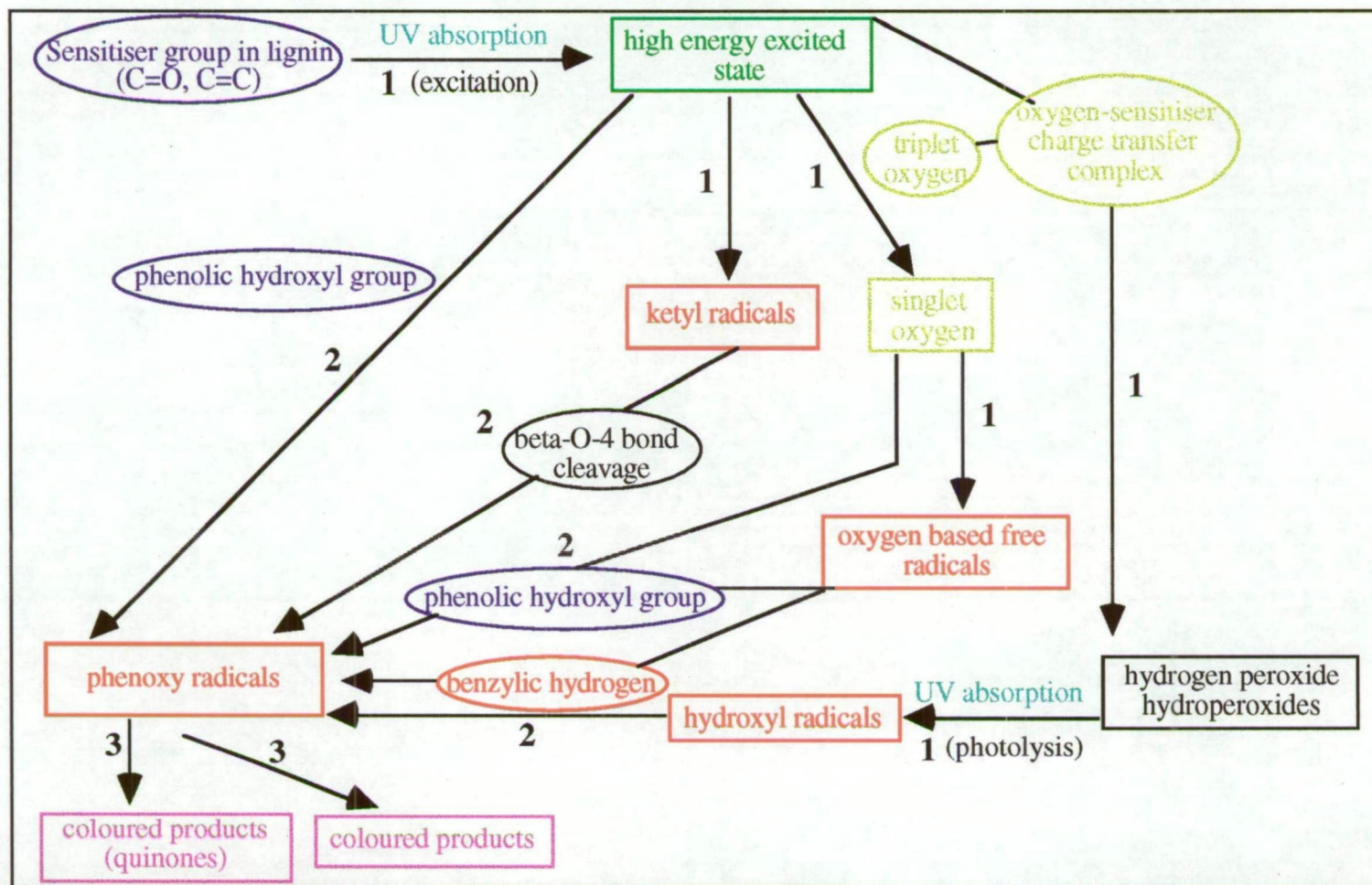
#### 1.3.1 Chemical modification, blocking or disruption of relevant functional groups

This option has the advantage that reversion would theoretically be stopped at one of its beginning stages. It was actually one of the first methods of inhibition studied. Authors as early as the 1940s employed several techniques to modify or block free phenolic hydroxyl groups in the hope that they would become impervious to further reaction, i.e. to hydrogen abstraction and subsequent radical formation. Methods employed to modify phenolic hydroxyl groups have included acetylation, methylation, benzylation and etherification. These are discussed below.

##### *Acetylation of phenolic hydroxyl groups*

Acetylation has been shown by several authors to incur an initial bleaching effect<sup>83,84</sup>, which is followed by effective inhibition of photo-induced reversion<sup>51,83,84</sup>. At high concentrations this treatment has even been shown to increase brightness during irradiation<sup>83,84</sup>. Analysis by Lorås<sup>83</sup> in 1968 showed that while some acetyl groups attached to benzene rings and side chains, the main proportion attached to carbohydrate groups not significantly involved in the photo-yellowing processes. Such non-specific attachment is one disadvantage of acetylation due to large portions of the acetyl groups being lost to non-inhibitory reactions. Lorås also suggested that acetylation may have changed the properties of the lignin such that the light-induced bleaching observed at high wavelengths was able to proceed at lower wavelengths. More recent work by Ek et al.<sup>84</sup> showed acetylation to be more effective when a higher chromophore content was originally present, i.e. acetylation was more efficient in stabilising unbleached pulp compared to its peroxide bleached counterpart. Ek et al. proposed that acetylation lead to two stabilisation mechanisms, one being acetylation of photo-reactive groups (i.e. blocking phenolic groups) and the other involving retardation of chromophore formation by the removal of quinone-type structures via reductive acetylation.





**Figure 1.3.** A summary of some possible inhibition methods and their target points, based on proposed mechanisms for photo-induced yellowing reactions of lignin-rich pulps and papers (1. Initiation steps (primary and secondary). 2. Formation of phenoxyl radical intermediates. 3. Formation of yellow species). Dark blue: Chemical modification of functional groups. Light blue: UV-absorbers. Green: Excited state quenchers. Yellow: Oxygen quenchers. Red: H-donors, radical scavengers. Pink: Removal of coloured products.

### ***Benzoylation of phenolic hydroxyl groups***

This method has resulted in a fair degree of inhibition<sup>51,47</sup>, with an initial bleaching observed<sup>47</sup>. Excess doses were required however and therefore it is also not an economically feasible approach to stabilise photo-induced reversion<sup>47</sup>.

### ***Etherification of phenolic hydroxyl groups***

Wallis and Wearne<sup>84a</sup>, and then later Janson and Forsskåhl<sup>3</sup>, showed that etherification of phenolic groups with alkene oxides had a stabilising effect. A more extensively studied inhibitor is modified polyethylene glycol (PEG), a commercially available, reasonably cheap, non-toxic polymer. It has been found to be an effective stabilising agent<sup>3,85,86,87</sup>, with stabilisation increasing with degree of polymerisation and large doses actually inducing photo-bleaching responses<sup>3,85,86</sup>. PEG also induces different stabilising efficiencies depending on the types of pulps used and whether or not they are bleached<sup>86</sup>. Its mechanism of inhibition is not fully understood, but suggestions have included exclusion of air by the polymer<sup>85</sup> and the involvement of ethene oxide radical intermediates<sup>3</sup>. Cole et al.<sup>87</sup> recently performed experiments that confirmed the existence of a chemical bond between a modified PEG and a model lignin compound, along with increased hydrophilicity. They suggested that phenolic hydroxyl groups were blocked by etherification with the modified PEG.

### ***Methylation of phenolic hydroxyl groups***

Methylation has been revealed to be a poor inhibition method for several reasons. It only partially stabilises against light-induced reversion<sup>51</sup> and doses required are large and economically not feasible<sup>47</sup>. Methylation has not appeared to affect the reaction kinetics of the yellowing processes<sup>68</sup> and its initial ability to stabilise declined upon further irradiation<sup>88</sup>.

### ***Other attempts to block functional groups***

#### ***Blocking of functional groups using metal ions***

Janson and Forsskåhl<sup>85</sup> have tried blocking functional groups (acidic groups like phenolic, carboxylic and sulpho groups) by formation of complexes or salts with metal ions. This treatment, however, did not result in stabilisation and some metal ions even contributed to the colour of the pulp. On the other hand a review paper by

Naqvi<sup>89</sup> showed that several chelated metal ions, particularly nickel- and zinc-chelate complexes, have been quite successful inhibitors of photo-degradation when applied to polymers. The mechanism of inhibition, while quite controversial, is not thought to be a blocking of functional groups, but rather a quenching of excited states or radical scavenging. It would therefore be interesting to see the results of an investigation carried out in a similar manner to Janson and Forsskåhls', but with the metal ions applied as chelate forms similar to those revealed by Naqvi.

#### *Blocking of hydroxyl groups using PVP*

Råtto et al.<sup>90,91</sup> studied commercially available PVP (polyvinylpyrrolidone). PVP has been reported to interact with phenolic hydroxyl groups in lignin via hydrogen bonds. Stabilisation of mechanical spruce pulps was achieved, the most efficient PVP compounds being the monomer (n-vinyl-2-pyrrolidone) and lowest molecular weight polymer (M.W. 10,000). They also caused an initial brightening effect. They found that PVPs interact with phenolic and/or alcoholic hydroxyl groups<sup>9</sup>, and their results suggested that PVP adsorbs onto a specific fraction of lignin which is closely associated with or bonded to the carbohydrates. Therefore PVP seems to act as an adsorbent specific for phenolic and/or alcoholic hydroxyl groups, thus retarding brightness reversion.

#### *Reduction of carbonyl groups using borohydride*

Carbonyl groups are thought to be involved in the initial phases of photo-reversion (see Section 1.2). Disruption of these groups has been tried by reducing them with borohydride, a known bleaching agent. Schmidt and Heitner<sup>68,92</sup> found that this treatment did not affect the yellowing reaction mechanisms, and its initial bleaching effect was lost during irradiation. They proposed that benzyl alcohols formed by borohydride reduction are rapidly oxidised back to carbonyl groups on irradiation.

Francis et al.<sup>88</sup> found that although inhibition was quite poor, it could be stabilised when borohydride reduction was followed by alkylation (e.g. methylation), thus deactivating both carbonyl and phenolic hydroxyl groups. This resulted in a synergistic effect for peroxide bleached TMP, but was only as effective as methylation alone for unbleached TMP<sup>88</sup>. When acetylation followed the reduction, little stability resulted<sup>84</sup>. Therefore, borohydride reduction had actually diminished the inhibition that had previously been observed for acetylation, discussed above. On the other hand, borohydride reduction followed by catalysed hydrogenation to eliminate aromatic conjugated double bonds gave good stability, more so for peroxide bleached milled wood lignin (MWL) than unbleached MWL<sup>93</sup>.

### 1.3.2 UV absorbers

UV absorbers are organic compounds able to absorb UV radiation and redistribute it as non-harmful thermal energy. Fornier de Violet et al.<sup>67</sup> showed that some UV absorbers, for example 2,4-dihydroxy-benzophenone, which is used in polymer stabilisation<sup>89</sup>, were also good inhibitors for lignin-rich pulps. Their mechanism is thought to involve rapid isomerisation of the excited states. Johnson<sup>2,26</sup> showed that some fillers and thin surface coatings containing  $\text{TiO}_2$ , (a strong absorber of UV light as well as scatterer of visible light), were beneficial to the stability of papers containing chemi-thermomechanical pulp (CTMP). He found that clay coated papers exhibited some stability but this was due to protection of the fibres rather than a strong UV absorption by the clay, so some reversion still occurred. The commercial filler  $\text{CaCO}_3$  which does not have UV absorbing ability but is a good light scatterer did not affect the chemistry of the reversion process but still preserved brightness to some degree. By replacing some of this filler with  $\text{TiO}_2$ , he was able to slow the reversion chemistry. Such coatings can substantially improve the brightness reversion stability of papers containing mechanical pulps by blocking some of the damaging UV light and also hiding the colour of yellowed fibres. As only thin surface coatings of  $\text{TiO}_2$ /clay are required it is a cost-effective mode of inhibition.

### 1.3.3 Excited state quenchers

Fornier de Violet et al.<sup>67</sup> showed that chain breakers, such as hindered phenols, HALS (hindered amine light stabilisers) and naphthalenic derivatives known to be good  $\alpha$ -carbonyl triplet quenchers, had detrimental or no effects. Such compounds are used as additives to protect synthetic polymers against oxidation. Recently Harvey and Ragauskas<sup>94</sup> investigated hexadienol. They found that photo-degradation of lignin was reduced by hexadienol, possibly because it quenches the excited states of lignin chromophores such as  $\alpha$ -carbonyl groups of phenacyl aryl ethers. 2,4-hexadienol and related unsaturated systems were effective additives for retarding photo-yellowing of hardwood peroxide bleached CTMP pulps (BCTMP). Although significant decreases in the rates of photo-yellowing were observed, improvements are still required. Hexadienol retarded one of the initial photo-chemical reactions that contributed to the photo-degradation of a MLC, probably by quenching the ketone excited state (carbonyl triplet state) and retarding a photo-induced bond cleavage. After further irradiation however, a lack of triplet state quenching (and therefore an increase in photo-cleavage) was observed. It was suggested that hexadienol also acted as a H-atom donor, with the resulting hexadienol radical resonance stabilised. Upon irradiation in the absence of lignin

(i.e. on a medium containing only cellulose), hexadienol produced only its starting isomer. In the presence of lignin (i.e. on BCTMP) however, it photo-isomerised to yield all four of its geometric isomers. Another suggestion as to its mechanism of inhibition was a termination of free radical propagation by H-atom donation. So it is possible that this species contains a dual mode of action, acting as both an excited state quencher and a hydrogen donor or radical scavenger. Ragauskas<sup>95</sup> also studied unsaturated compounds as reversion inhibitors. He found that a degree of stabilisation was possible by impregnating mechanical pulps with cyclic and acyclic diene compounds (antioxidants), with efficiency of stabilisation dependent on the structure of the diene. *Trans,trans*-2,4-Hexadien-1-ol revealed good inhibition, but its thermal stability was questionable and long-term reversion was accelerated. So dienes are promising, but a major drawback is their contribution to thermal reversion.

#### **1.3.4 Oxygen quenchers / singlet oxygen quenchers**

The known singlet oxygen quencher DABCO (1,4-diazabicyclo-2,2,2-octane) has been studied as a possible inhibitor<sup>65,85</sup>. Whereas Janson and Forsskåhl<sup>85</sup> found it to actually darken pulp, Wang et al.<sup>65</sup> found that it decreased the photo-oxidative degradation of peroxide bleached MWL to about 72%. This could be explained by the different pulp types used by each group of researchers. Experiments by Wang et al. support the view that DABCO inhibits photo-degradation, or light-induced depolymerisation, by quenching singlet oxygen. This prevents the formation of oxygen-based free radicals that can abstract benzylic hydrogen, subsequently preventing the formation of phenolic groups which are oxidised to coloured species.

#### **1.3.5 Hydrogen-donors (radical scavenging antioxidants)**

To date the use of hydrogen donors and radical scavengers seems to be the most extensively studied approach to inhibiting photo-induced reversion. Some hydrogen donating compounds which have been studied as possible reversion inhibitors are acetic acid, several sulphur-containing compounds, and some phosphorous compounds. Discussions of the inhibition abilities found for these compounds, and proposals pertaining to their modes of action, are given below.

##### ***Ascorbic acid***

In 1977 Schuler<sup>96</sup> showed that phenoxyl radicals could rapidly oxidise ascorbate anions resulting in the anion being fairly non-reactive. Therefore addition of these anions may be one way of selectively removing phenoxyl radicals, and inhibiting their further reaction towards coloured species. These anions were shown to also

remove some other radicals, albeit slowly. However, further radicals studied did not react with the ascorbate anion at all. From the above findings Schuler suggested that in a lignin-photo-yellowing system radical removal via this method would probably be incomplete, and thus reversion inhibition would also be incomplete. Although he did not perform the experiments with the aim of inhibiting reversion, but rather as a way of "separating" radicals in order to investigate them further, he had still introduced a way to remove phenoxyl radicals, a major participant in the photo-yellowing process. Several researchers have since studied ascorbic acid as a possible inhibitor. It is a known common hydrogen donor or radical scavenging antioxidant able to scavenge both ketyl and phenoxyl radicals<sup>43</sup>, and it did indeed give good stabilisation against photo-induced reversion<sup>3,85</sup>. Its effect was short-lived<sup>68</sup>, however, and it also lost its activity on storage<sup>67</sup>. Schmidt and Heitner<sup>68</sup> suggested that ascorbic acid could scavenge phenoxyl radicals, while becoming oxidised itself. It could also inhibit the formation of aromatic carbonyl or ketone groups either by inhibiting the oxidation of benzyl alcohols or by photo-chemical reduction. They found that bleached TMP treated with ascorbic acid underwent some photo-bleaching of a chromophore absorbing around 350nm, possibly a stilbene<sup>92</sup>.

### *Sulphur-containing compounds*

Sulphur-containing compounds, or mercaptans, are possibly the most studied potential photo-reversion inhibitors so far. Mercaptans are efficient hydrogen-donors<sup>9</sup>, as they contain a highly reactive -SH group that can undergo cleavage of the relatively weak S-H bond ( $399\text{kJ}\cdot\text{mol}^{-1}$  compared to  $462\text{kJ}\cdot\text{mol}^{-1}$  for O-H bonds). Mercaptans can also react with oxygen or other radicalising molecules, and are also good quenchers of the photo-excited state (albeit slow ones). Having this property, they should trap radical species without interfering with the actual reaction. Furthermore mercaptans are also good nucleophilic and reducing species<sup>98</sup>.

Several sulphur-containing compounds have been shown to act as antioxidants for synthetic polymers and other organic materials<sup>67,97</sup>. For example 1-dodecanethiol is used in the rubber industries to prevent oxidation and UV modification of polymers<sup>98</sup>. In 1985 Duffield and Lewis<sup>99</sup> reported that some sulphur-containing compounds, including the mercaptan thioglycolic acid, were also effective in stabilising wool against light-induced yellowing with high levels actually enhancing the photo-bleaching of wool observed under blue light. It was proposed that they acted via antioxidant processes, removing hydroperoxides which could otherwise initiate reactions leading to yellow products. It was also suggested that the mercaptans bleached yellow products. In 1987 Cole et al.<sup>97</sup> produced a paper on the

application of such compounds as inhibitors for lignin-containing pulp and paper reversion, and since then several authors have studied these compounds as well. The following discussion will show what has been discovered about these compounds, along with empirical and theoretical reaction mechanisms.

The sulphur-containing compounds most studied so far have been the thiols, which contain free SH end groups. They have been shown to be effective in both bleaching and stabilising pulps against light-induced yellowing. Thiols which have been studied as potential inhibitors include 1-thioglycerol<sup>3,85,97</sup>, glycol dimercaptoacetate or ethylene glycol bithioglycolate (EGB)<sup>97,100</sup>, mercaptoacetic acid or thioglycolic acid<sup>70</sup>, and 3-mercapto-1,2-propanediol<sup>100</sup>. The relatively long-chained 1-dodecanethiol has also been studied, but conflicting results have been reported. Whereas work by Daneault et al.<sup>98</sup> revealed this compound to be highly efficient in both bleaching and stabilisation, experiments by Pan and Ragauskas<sup>100</sup> showed it to contain no bleaching or stabilising qualities. In fact, in Pan and Ragauskas' study 1-dodecanethiol appeared to actually increase photo-induced discolouration rather than inhibit it. Differing pulps and experimental conditions may explain this discrepancy. Preliminary tests conducted by the author of the present thesis on the stabilisation ability of mercaptans (which are unpublished and omitted from this thesis), concurred with the findings of Pan and Ragauskas. That is, 1-dodecanethiol was totally ineffective as a bleaching agent, and increased rather than inhibited the photo-induced reversion of both TMP and BTMP handsheets. This result, being contradictory to the findings of Daneault et al., prompted further tests on the 1-dodecanethiol sample. NMR scans revealed that it had completely oxidised on storage. (Unfortunately, while in transit this compound had been stored improperly with respect to the manufacturer's specifications.) Consequently, the chemical was discarded and further work halted.

Despite their high efficiency in inhibiting reversion, several thiols have been found to lose their effectiveness on long-term storage. For example EGB and 3-mercapto-1,2-propanediol only retarded the natural reversion that occurs during storage to a small degree, and mercapto-carboxylic acids had a detrimental effect during long-term storage. It is possible that the mercaptans may react with oxygen and radicals generated by lignin autoxidation reactions, reducing the amounts of the thiol additives present on the surface of a handsheet during long term storage<sup>100</sup>.

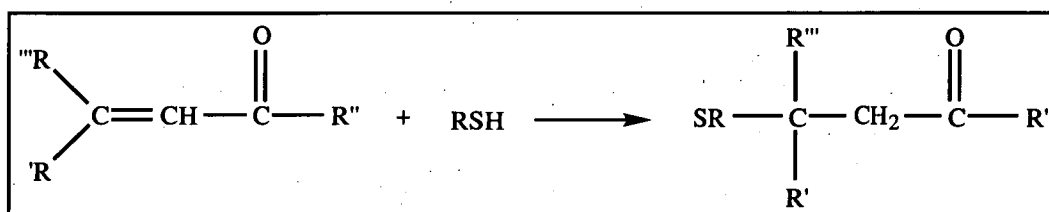
Sulphoxylates have also been shown to possess both bleaching and stabilising ability. For example, rongalite, studied by Fornier de Violet et al.<sup>67</sup> was shown to exhibit bleaching (possibly due to reduction of carbonyl and quinoidic groups), and stabilisation. The stabilising efficiency was short-lived, however, with respect to



post-aging. Thioethers with alpha thiol groups and methylenic hydrogens also exhibited good stabilisation ability, but lacked a bleaching effect<sup>67,97</sup>. The acid group of these compounds was found to be important as when it was removed (i.e. the salt structure was used instead, or the acid group was esterified) there was a loss in stabilising power<sup>67</sup>. Sulphur-containing compounds found to exhibit neither bleaching nor stabilising ability included sulphoxides and sulphones<sup>97</sup>. Cole et al.<sup>97</sup> also found disulphides to be ineffective, but Pan and Ragauskas<sup>100</sup> found them to give moderate inhibition which was sustainable on long-term storage, possibly due to radical scavenging ability. Again the discrepancies could be accounted for by the different pulps, experimental conditions and disulphides studied.

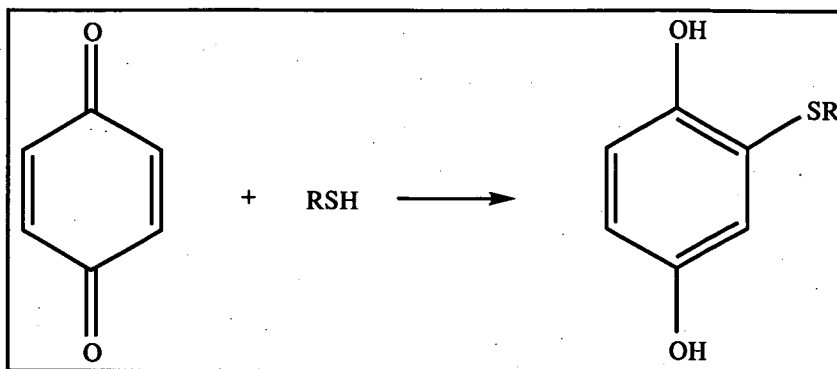
The mechanisms by which thiols inhibit reversion are not well understood, but several proposals have been made. In earlier work by Kutney<sup>101</sup> on the bleaching action of thiols, several mechanisms were suggested, including thioacetal formation (whereby C=O bonds are destroyed), Michael-type addition reactions (whereby C=C bonds are destroyed), and reduction of benzoquinones to hydroxyquinones. Cole et al.<sup>97</sup> suggested that the bleaching action be predominantly attributed to free thiol groups, with Michael-type addition of the thiol groups to  $\alpha,\beta$ -unsaturated keto structures and quinones, thereby removing such coloured species. This theory has been generally accepted by most authors.

Cole et al. also proposed mechanisms for stabilisation which were similar to the bleaching reactions. Inhibition could occur by Michael-type addition of thiols to  $\alpha,\beta$ -unsaturated keto structures, thus preventing further reaction of these species to quinones. Stabilisation could also occur via removal of quinones as they form through Michael-type addition reactions. This is not considered a true inhibition, as the yellow products still form. These two possibilities are shown in the diagrams below:



Michael-type addition of thiols to  $\alpha,\beta$ -unsaturated structures<sup>97</sup>.

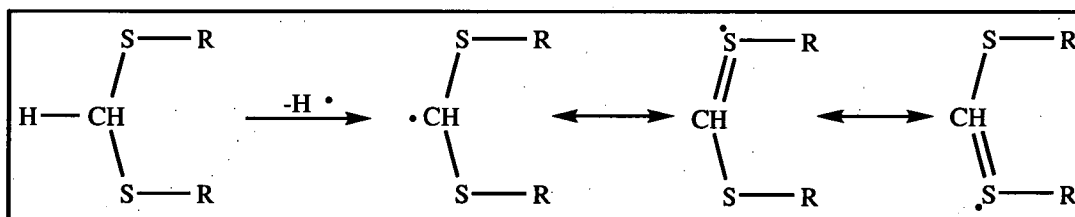




Michael-type addition of thiols to quinones<sup>97</sup>.

Studies by Pan and Ragauskas<sup>100</sup> supported the occurrence of Michael-type addition reactions of thiols when applied to mechanical pulps. They studied the binding of thiol groups (using EGB) to lignin during irradiation, and found that as irradiation proceeded more sulphur groups became chemically bonded, or strongly associated to the lignin. That is to say, sulphur became less extractable. On non-irradiated thiol-bleached handsheets, most of the sulphur was extractable, suggesting that the irradiation altered the nature of the sulphur present. This sulphur added to lignin during irradiation, resulting in stabilisation.

A third mechanism, proposed by Cole et al.<sup>97</sup>, involved hydrogen donation to intermediate radicals, preventing their further reaction, (at least for the case of thioethers with methylene groups or labile hydrogen atoms)<sup>67,97</sup>. Antioxidation would be effective via this mechanism, as the radicals produced by the abstraction of hydrogen would be resonance stabilised, as shown below:



Resonance stability of thio radicals after hydrogen donation<sup>97</sup>.

Experiments by Wang et al.<sup>65</sup> supported the hydrogen donation mechanism suggesting that thiols inhibit the oxidation of phenolic groups by quenching the phenoxyl free-radicals formed, without actually preventing the photo-degradation of lignin. Zhang & Gellerstedt<sup>70</sup> looked at the role of stilbene structures in photo-yellowing, and the effect thiols had on them. Their results also supported hydrogen

donation mechanisms. They suggested that by hydrogen donation and subsequent addition to the stilbene double bond, thiol groups could be used to capture all radical species formed, thus preventing the formation of coloured products. Proton abstraction from the thiol group produced thiol radicals, which subsequently added to the stilbene double bond in a radical chain reaction.

Daneault et al.<sup>98</sup> found the bleaching and inhibition effects to be dependent on the size of the mercaptan, indicating the inhibition process is physical rather than chemical. Straight chain thiols were more efficient than aromatic ones and the longer the molecule chain the more efficient was its stabilisation. Treatments on BTMP resulted in a better inhibition than treatments on TMP or CTMP handsheets, possibly due to the peroxide bleaching having increased the accessibility of reaction sites within the fibre matrix, and thus allowing the mercaptans to react more with the chromophores within the pulp. It is known that peroxide bleaching increases the amount of phenolic hydroxyl groups in the pulp. The higher efficiency of mercaptans on BTMP, therefore, may be due to their reaction with phenoxide radicals generated from the phenolic hydroxyl groups. Being trapped, they could then hinder oxygen diffusion, thus reducing the process of photo-oxidative colour reversion<sup>98</sup>.

Cole and Sarkanen also found strict steric requirements for stabilisation, but found that inhibition became worse as the mercaptan became bulkier<sup>97</sup>. In fact when they derivatised mercaptans with PEG, (discussed above as being a more efficient inhibitor as the degree of polymerisation or size increased), they found that stabilisation decreased as the chain length was increased. They also found that stabilisation depended not only on the presence of functional groups like thiol or thioether groups, but also on the structure of the rest of the molecule. For example, compounds with the mercapto group in an alpha position afforded the best inhibition, and ester derivatives (e.g. EGB) were better inhibitors than their acid counterparts (e.g. Thioglycolic acid).

### ***Phosphorous compounds***

Fornier de Violet et al.<sup>67</sup> studied some phosphorous compounds with hydrogen donating ability. Of the compounds studied only hypophosphite proved to be a good stabiliser, probably because of its good reducing properties.

### 1.3.6 Removal of coloured species

This mode of inhibition has not been addressed in its own right, but some inhibitors discussed above may exhibit dual roles that include removing coloured species as they form. For example it has been suggested that some of the thiols discussed above may prevent photo-yellowing to a degree, as shown above, while also inhibiting photo-yellowing by removing coloured quinone species as they form. Acetylation discussed above may also have a dual role, inhibiting reversion by blocking phenolic groups while also removing quinone-type structures via reductive acetoxylation<sup>84</sup>.

### 1.3.7 Miscellaneous

Other compounds shown to be effective stabilisers include some carbohydrates (free sugars and alditols) and nitrogen-free complexing agents such as tartaric acid and gluconolactone<sup>3,85</sup>. Polyethers like Polytetrahydrofuran (PTHF) protected lignin-containing products against light-induced and heat-induced colour reversion, but more than half of their effect was exerted before aging. They also reduced inter-fibre bonds and therefore tensile strength. The mechanism for this is not fully understood, but could possibly involve PTHF a) forming complexes with sensitive groups in lignin, b) exerting antioxidative effects, c) creating changes in the migratability of components in the yellowing processes, or d) protecting reactive sites against the penetration of oxygen. Of several other polymers tested only polyvinyl alcohol (PVA) inhibited reversion<sup>102</sup>.

### 1.3.8 Combinations

Combinations of the discussed modes of inhibition have also been studied in attempts to target more than one yellowing step simultaneously, thus creating a more efficient inhibition. In some such studies synergistic inhibition using combinations has been found, but not in all cases. As discussed above borohydride reduction coupled with acetylation, hydrogenation, methylation and others improved stabilisation in some cases, but did not always give positive results<sup>84,88,93</sup>. PEG coupled with EGB resulted in no enhancement of stabilisation efficiency<sup>97</sup>. Despite this, PEG coupled with other radical scavenging antioxidants gave promising results. For example, combinations of PEG with ascorbic acid or mannitol<sup>85</sup> and PEG with 1-thioglycerol and ascorbic acid<sup>3</sup> gave very good stabilisation, possibly due to

simultaneous blocking of phenolic hydroxyl groups and radical scavenging. Addition of polytetrahydrofuran followed by sizing with PEG has also been shown to give a high degree of stability<sup>102</sup>.

Pan et al.<sup>103</sup> studied combinations using three radical scavengers (EGB (thiol), 3,3'-dithiodipropionic acid (disulphide) and ascorbic acid) and two UV absorbers (5-phenylpenta-2,4-dienoic acid (diene) & 2,4-dihydroxy-benzophenone). Synergistic stabilisation was found for ascorbic acid and EGB combinations, with the yellowing observed for ascorbic acid on long-term storage even being prevented. Thus it appears that although both EGB and ascorbic acid act as scavengers, they act on (in part at least) different components of the overall reversion process. The thiol could also act as a H-donor or radical scavenger, quenching reactive radical intermediates which contribute to the autoxidation of ascorbic acid to yellowed products on long term storage. Ascorbic acid in conjunction with the disulphide or the diene exhibited no synergism and the long-term yellowing of ascorbic acid was unaffected by the disulphide. EGB combinations with benzophenone or the diene were synergistic, and EGB combined with both benzophenone and ascorbic acid was the best combination studied. All cases of synergistic stabilisation required lower doses of the inhibitors than single applications allowed for effectiveness. Thus combinations would certainly be a more cost-effective alternative to single inhibitor applications.

### 1.3.9 Summary

In summary, current research into inhibition of photo-induced reversion of lignin rich pulps and papers is extensive and diverse. Many inhibitors have been discovered, but despite all the research that has been done, a suitable candidate for commercial use has yet to be designed. The most common limitation has been cost-effectiveness. Too little is also known, however, about how each compound inhibits reversion. Although suggested mechanisms of inhibition are sound, there has been little experimental evidence to confirm many of these mechanistic proposals. Even where experiments have supported theories regarding one pathway, it is likely that further processes also occur simultaneously.

## 1.4 Parameters Used to Monitor Photo-Induced Reversion and its Inhibition

There are currently a large number of parameters that can be used for monitoring the extent of photo-induced reversion of lignin-rich pulps and papers, along with its inhibition. These include measurements of ISO brightness, post colour numbers (PC), yellowness indices (YI), and the tristimulus colour coordinates ( $L^*$ ,  $a^*$  and  $b^*$ ). Formulae based on these parameters have also been constructed to measure the percentages of stabilisation resulting from treatment with inhibitors. Techniques used to gauge at least some of the chemical changes occurring during photo-induced reversion and its inhibition have mostly involved calculations of the absorption coefficients,  $k$ , and construction of diffuse reflectance UV-visible absorption spectra, absorption difference spectra, or action spectra. Many more conventional chemistry techniques have also been used, however, including MS, NMR, ESR, FTIR, and Raman spectroscopy. Until standard procedures are specified, any number of these parameters or techniques can be used. Throughout this thesis the tristimulus colour parameters  $L^*$ ,  $a^*$  and  $b^*$  were chosen to monitor the extent of discolouration caused by photo-induced reversion for samples treated with inhibitors and samples not treated with inhibitors. The absorption coefficients,  $k$ , were calculated to monitor the changes in the content of chromophoric groups in these samples, and diffuse reflectance UV-visible absorption and absorption difference spectra were constructed to provide further insight into the chemical changes that may have occurred. A brief introduction of each of these parameters and techniques is given below, including discussions on the reasons for their selection and ways of measuring them. In some cases GC-MS were also conducted to aid in chemical analyses. As this is a standard tool for chemical analysis, however, it is not discussed further in this chapter.

### 1.4.1 The tristimulus colour parameters, $L^*$ , $a^*$ and $b^*$

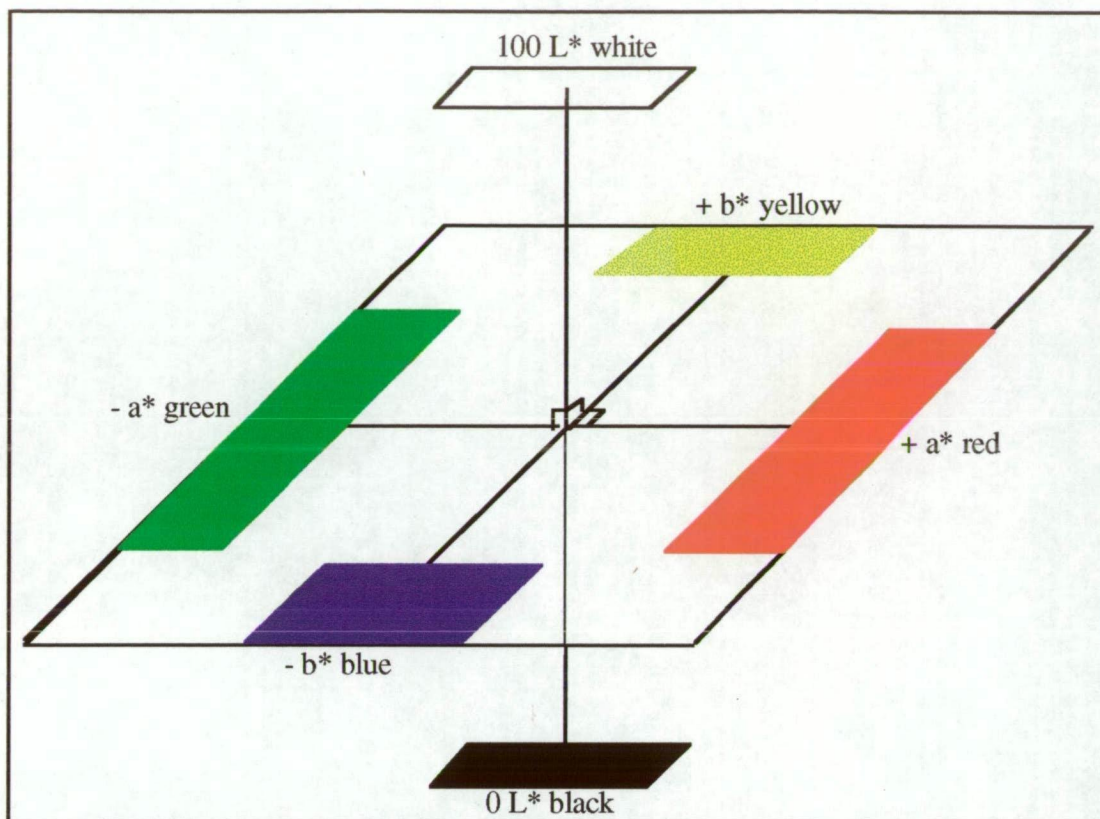
The tristimulus colour parameters  $L^*$ ,  $a^*$  and  $b^*$  were selected to monitor the extent of colour reversion and its inhibition due to their close correlation to real perceived colour. Calculating these parameters involves applying a complex series of mathematical functions and this is generally performed computationally by the measuring device, which for this thesis, was an Elrepho datacolor 2000 spectrophotometer. The mathematics will not be described in detail here, but the interested reader is referred to an article by B. Jordan and M. O'Neill<sup>104</sup> where the derivations and origins of these parameters are clearly and concisely described. The main points worth noting are as follows:

a. The parameters are derived from the CIE tristimulus functions, which are spectral sensitivity functions of stimuli from the three photo-receptors in the human eye. Thus they are a representation of colour as it is truly observed<sup>104</sup>.

b. Deriving these parameters involves multiplying reflectance values of a sample by the tristimulus functions, and then integrating the products over all wavelengths of visible light<sup>104</sup>. These parameters are therefore a more accurate measure of colour changes in a paper sample than parameters which derive their values from only a finite spectral range. For example, one conventional measure of the optical quality of paper is ISO brightness, which derives its value from the reflectance of a sample at only a finite spectral region centred around 457nm (in the blue region of the visible spectrum)<sup>92,105</sup>. Reflectance spectra of BTMP, however, has revealed that the strongest absorption (i.e. the smallest reflectance) occurs at wavelengths below 400nm, as the absorption maxima of many structural units in lignin occur below this point. Therefore ISO brightness measurements represent only the tail ends of absorption peaks, with several absorption maxima of important chromophores possibly going unrecognised<sup>92</sup>. Furthermore, unlike  $L^*$ ,  $a^*$  and  $b^*$ , ISO brightness is not a direct measure of any visual property as it is not related to any system of colourimetric measurement, and therefore has no foundation in perceptual psychology<sup>105</sup>.

c. The final steps in deriving the CIE  $L^*$ ,  $a^*$  and  $b^*$  parameters involve separating the white-black (or achromatic) continuum from the hue, or colour components. This results in a grey-scale continuum (the  $L^*$  axis), which is perpendicular to a plane of hue and purity, (called the chromaticity diagram), which specifies the colour of a sample. After further mathematical manipulations to the chromaticity diagram, the resultant perpendicular  $a^*$  and  $b^*$  axes produce meaningful measures of colour, ranging from red to green (the  $a^*$  axis) and yellow to blue (the  $b^*$  axis). The resultant 3-D map of the CIE  $L^*a^*b^*$  colour space is simple, and can be easily applied to visualised colour. This colour space is shown in Figure 1.4<sup>104</sup>.

For the whole of this thesis, tristimulus colour parameters were measured using an Elrepho datacolor 2000 spectrometer.



**Figure 1.4.** The 3-D colour space formed by the CIE tristimulus colour parameters  $L^*$ ,  $a^*$  and  $b^*$ .

#### 1.4.2 The absorption coefficient, $k$

One complication when using the tristimulus colour parameters  $L^*$ ,  $a^*$  and  $b^*$  to monitor the extent of reversion may arise when comparing materials that have contrasting initial colours. For example a highly bleached TMP handsheet may be more sensitive to small increases in colour than an unbleached and already coloured handsheet. Thus reversion-induced changes in the colour parameters may be amplified for bleached handsheets, and minimised for unbleached handsheets. A knowledge of the actual increase in the chromophore contents of two contrasting sheets would therefore provide a more reliable basis for making constructive comparisons. This can be achieved in part by calculating the changes in the absorption coefficients,  $k$ , as this parameter is directly proportional to the concentration of chromophores actually present in the sheet being tested<sup>92</sup>. One limitation of this is that changes in  $k$  only reflect changes in the content of chromophores which absorb at the wavelength for which  $k$  is measured, i.e. it does not provide information on chromophoric changes occurring outside the range of measurement. Nevertheless, it is still a more accurate indication of actual chromophoric changes at a given wavelength than the visual parameters discussed



above. The relationship between the absorption coefficient and the concentration of chromophores is shown below:

$$k_{\lambda} = 2\epsilon_{\lambda}C$$

where  $k$  = the absorption coefficient;

$\epsilon$  = the extinction coefficient;

$C$  = the concentration of the absorbing species (chromophores);

and  $\lambda$  = the wavelength at which  $k$  is measured.

The absorption coefficient of optically thick paper samples can be calculated from measurements of reflectances at a particular wavelength, by applying the Kubelka-Munk remission function which is shown below<sup>92,106,107</sup>:

$$\frac{k}{s} = \frac{(1 - R_{\infty})^2}{2R_{\infty}}$$

$$\text{where } s = \frac{R_{\infty}}{B(1 - R_{\infty}^2)} * \ln \left[ \frac{R_{\infty}(1 - R_{\infty}R_0)}{(R_{\infty} - R_0)} \right];$$

$k$  = the specific absorption coefficient;

$s$  = the specific scattering coefficient;

$R_{\infty}$  = the reflectance of the sample over a background consisting of the same material with thickness such that the supporting background has no optical effect;

$R_0$  = the reflectance of the paper over a standard black background;

and  $B$  = the basis weight of the sample.

The relevant reflectance measurements in this thesis were all performed on an Elrepho datacolor 2000 spectrometer. All measurements were performed at a wavelength of 457nm, which in the case of  $R_{\infty}$  coincides with ISO brightness.

#### 1.4.3 Diffuse reflectance UV-visible absorption spectra and difference spectra

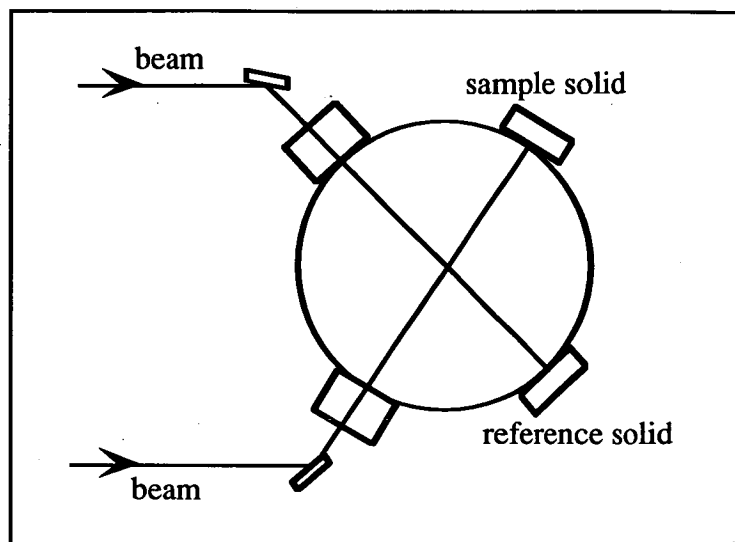
Diffuse reflectance UV-visible absorption spectra have become a widespread analytical tool for use in both bleaching and reversion paper chemistry. The basic skeleton of lignin is colourless and reveals absorption peaks in the UV region of the spectra only. Upon conjugation, however, this absorption is shifted towards the visible region of the spectrum (i.e. to higher wavelengths). More specifically, the introduction of conjugation produces yellow chromophoric groups which absorb higher wavelength radiation in the blue (the conjugate colour of yellow) region,



between 400 and 500nm. Thus the production or destruction of chromophoric groups in lignin can clearly be observed as changes in the visible region of an absorption spectra. The theory behind these spectra comply with the conventional absorption spectroscopy theory, which is found in most standard chemistry texts. That is, chemical species absorb photons of different energies (i.e. at different wavelengths), depending on their chemical structure. Thus the UV-visible absorption spectra of paper can also reveal information on the chemical species in a sample by matching the positions of its constituent peaks to known characteristic absorption patterns of functional groups and chemical compounds. This is somewhat limited, however, as many chemical structures absorb in similar spectral regions, and vibronic coupling often gives rise to broad peaks. Therefore an absorption spectrum may contain overlapping peaks which are difficult to distinguish and interpret<sup>107</sup>. Nevertheless, comparisons between spectra or difference spectra can still provide useful information on whether two processes have resulted in similar or distinct chemical changes. For example, if irradiation of two different samples resulted in similar discolouration and increases in the content of chromophores, but revealed different UV-visible absorption spectra, then it could be concluded that distinct chemical changes had occurred.

In paper chemistry the absorption spectra as measured throughout this thesis are referred to as *diffuse reflectance* absorption spectra. This is because the absorption values of paper samples were measured indirectly, with the aid of a special attachment to the spectrophotometer called a solid diffuse reflectance, or integrating, sphere. This sphere is coated on the inside with a standard pure white substance (for example MgO) which ideally exhibits 100% reflecting properties. There are two slots on the sphere, one being a reference port and the other being a sample port. The reference port usually contains a standard white reflector. Radiation enters the sphere and is reflected ideally around the entire inner surface in such a way that the only absorption that occurs is by the sample in the sample port. The output radiation therefore consists entirely of the input radiation minus that which was absorbed by the sample. If difference spectra are required, a reference sample is positioned in the reference port. The resultant output is then related to the differences in absorption between the sample and the reference sample. The sphere attachment is shown in Figure 1.5.

All UV-visible absorption spectra presented in this thesis were measured using a Varian DMS 100 UV-visible spectrophotometer fitted with an integrating sphere. The results were downloaded as transmittance (T) values by a computer program and then transformed into absorption (A) units using the relationship<sup>108</sup>  $A = -\log T$ .



**Figure 1.5.** The diffuse reflecting sphere attachment used for measuring the absorption spectra of solid samples (taken from the Varian DMS 100 UV-Visible Spectrophotometer Operating Manual. Technical Author E. Rothey, Publication Number 85-100527-00 December 1982, Page 16.).

## **CHAPTER 2**

# **FINDING A SUITABLE LIGHT SOURCE TO ARTIFICIALLY INDUCE PHOTO-REVERSION OF TMP**

### **2.1 Introduction**

Section 1.1 introduced the aim of this project, which is to investigate the inhibition of light-induced reversion of TMP. Before this could be achieved however, a reasonable induction of the photo-reversion phenomena was required. Experiments using natural conditions are time consuming, and fluctuations in weather conditions are totally unreliable for the commencement of a long term project. Thus artificial simulations are the only logical course of action. This chapter explores the ability of several commercially available light sources to simulate the photo-induced reversion caused by natural sunlight.

In Section 1.1 the factors affecting photo-reversion of lignin-rich pulps and the spectral regions involved in this process were introduced. It was reported that in natural conditions a yellowing and bleaching response occurred simultaneously, with yellowing more predominant. The spectral regions involved in these photo-reactions included the UV region (300-400nm) responsible for the yellowing and longer wavelengths (400-500 and 600nm) responsible for the bleaching. Thus light sources were chosen for their potential for containing these spectral regions, and for simulating photo-reactions proportional to those experienced under natural sunlight conditions. A neat UV source was also tested for its surety in producing yellowing in case the “natural” simulations proved inadequate, as it is the yellowing reaction which is of primary concern in the reversion of TMP. The light sources studied are listed below;

1. An 18W Colour 11 Lumilux® Daylight tri-phosphor tubular fluorescent tube, advertised as simulating natural daylight. Its spectral distribution over the visible wavelengths (cited in the catalogue<sup>109</sup>) was diverse, but details of the UV region were unavailable. This light source is referred to as the “artificial daylight” tube throughout the rest of this chapter.

2. A 300W Ultravitalux sunlamp, advertised as closely resembling the radiation of the sun in high mountain areas. The radiation is generated by a quartz

discharge tube and a tungsten filament. The bulb is custom made, using a special glass which transmits only that part of the output which is part of the solar spectrum (i.e. 300nm and above). The effects of UV radiation are intensified due to simultaneous IR radiation. A complete spectrum from the catalogue, ranging from 300 to 2000nm, revealed a broad spectral range<sup>110</sup>.

3. A blacklight blue fluorescent tube generating UV rays at a peak of 360nm. A special dark blue glass filter eliminates most visible light<sup>109</sup>.

It should be noted that another light source currently popular for paper reversion studies is the xenon lamp, with a borosilicate filter to eliminate wavelengths below 300nm, reported to have a close match to the spectral energy distribution of daylight<sup>2,9</sup>. These lamps, however, were not easy to obtain commercially. They are also expensive and are known to produce very high temperatures.

Each light source was tested for its ability to induce photo-reversion on both thermomechanical pulp (TMP) and peroxide bleached TMP (BTMP). TMP was tested as it is the primary source of pulp for which photo-reversion is a major problem. For commercial lignin-rich papers however it is currently standard practice to bleach this pulp with hydrogen peroxide prior to sheet formation. Thus BTMP was also tested due to its relevance to industry. The chemical changes induced in these pulps by each light source were compared with those induced by natural sunlight, and spectral energy distributions of the lamps were also compared to that of sunlight.

Before commencement of the irradiations two potential complications required consideration. The first was interference by metal ions which could be present in the TMP. It was pointed out in Section 1.1 that these ions could interfere with photo-reversion by acting as catalysts during the process, or by forming coloured complexes which may add to the final colour of the pulp. To reduce this possible interference all pulps were pre-treated with the chelating agent DTPA prior to handsheet formation or peroxide bleaching. This was assumed to remove the majority of metal ions pre-existent in the pulp.

The second potential interference was thermal reversion, which was also discussed in Section 1.1. The main concern is that photo-reversion and thermal reversion are visually indistinguishable on the surface of the paper (both having darkening and yellowing effects), even though they are believed to follow different reaction pathways. Two differences, however, can aid in distinguishing these two reversion types. First, thermal reversion can penetrate paper, whereas photo-induced reversion is a surface only effect. Thus the underside of an exposed handsheet can be used to

distinguish if the yellowing is due to thermal or photo-reversion. The second important distinction is that while photo-reversion can occur at room temperature, thermal reversion can only occur to a discernible degree at elevated temperatures. Thus temperatures were monitored throughout the irradiations to gauge the potential of thermal reversion occurrence. When it was suspected, further tests were performed on the underside of exposed handsheets, to check if it had actually occurred (especially for the Ultravitalux sunlamps, which emitted the most amount of heat).

## **2.2 Experimental Design and Conditions**

### **2.2.1 Preparation of handsheets**

All pulps (TMP courtesy of Australian Newsprint Mills, Boyer) were pre-treated with 0.5% o.d. DTPA at 1% consistency for 75 minutes at 57°C, and then washed thoroughly with distilled water. Half the pulp was bleached with 3% H<sub>2</sub>O<sub>2</sub>, 2.4% NaOH, and 3% sodium silicate (100% chemical), at a consistency of 14% for 2 hours at 65°C. The pulp was then washed thoroughly with distilled water. The pH was adjusted to  $4.5 \pm 0.1$  and handsheets then made to approximately 60-65 g/m<sup>2</sup> following standard procedure without white-water recirculation, or capture of fines.

To check for thermal reversion with the Ultravitalux lamps, thicker handsheets were made to approximately 149 g/m<sup>2</sup>.

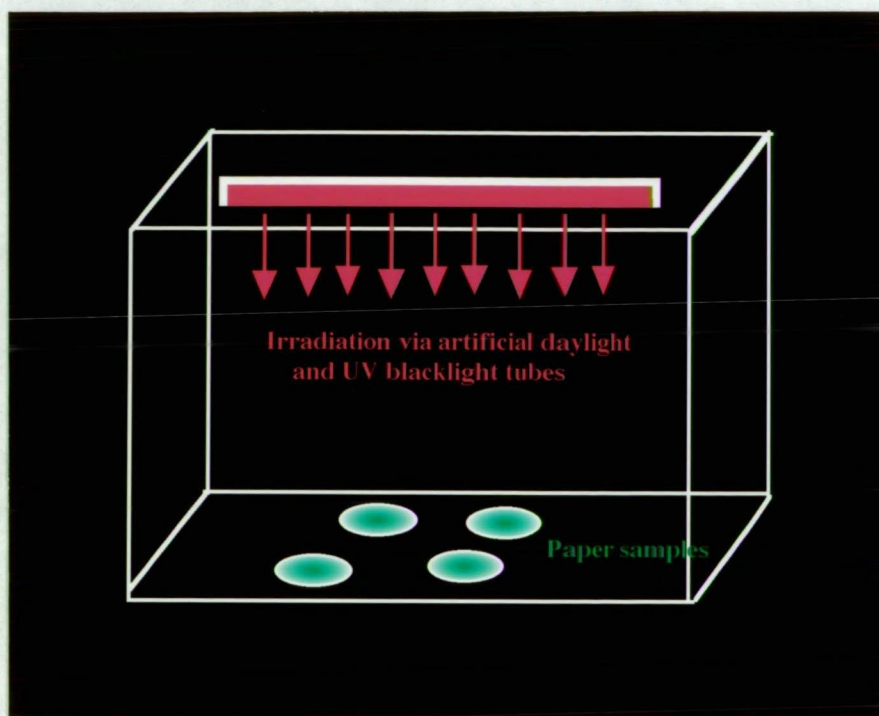
### **2.2.2 Irradiation set-up**

#### ***Natural sunlight***

Sunlight irradiations were performed between mid-morning and afternoon on clear days by laying samples out in the open for identical time periods to the artificial irradiations.

#### ***Artificial daylight and UV tubes***

The artificial daylight and UV tubes were identical in shape so their set-ups were identical. Each light tube was attached to the roof of a matt black enclosure (dimensions 38 by 99 cm<sup>2</sup>) to avoid light scattering, and thermometers were placed inside to monitor temperature during irradiation. As both of these light sources consisted of a fluorescent tube that extended over the length of the chamber, they were assumed to exhibit a uniform irradiation over the sample surface. The set-up is shown in Figure 2.1.



**Figure 2.1.** Irradiation chamber containing an artificial daylight tube or a UV blacklight tube.

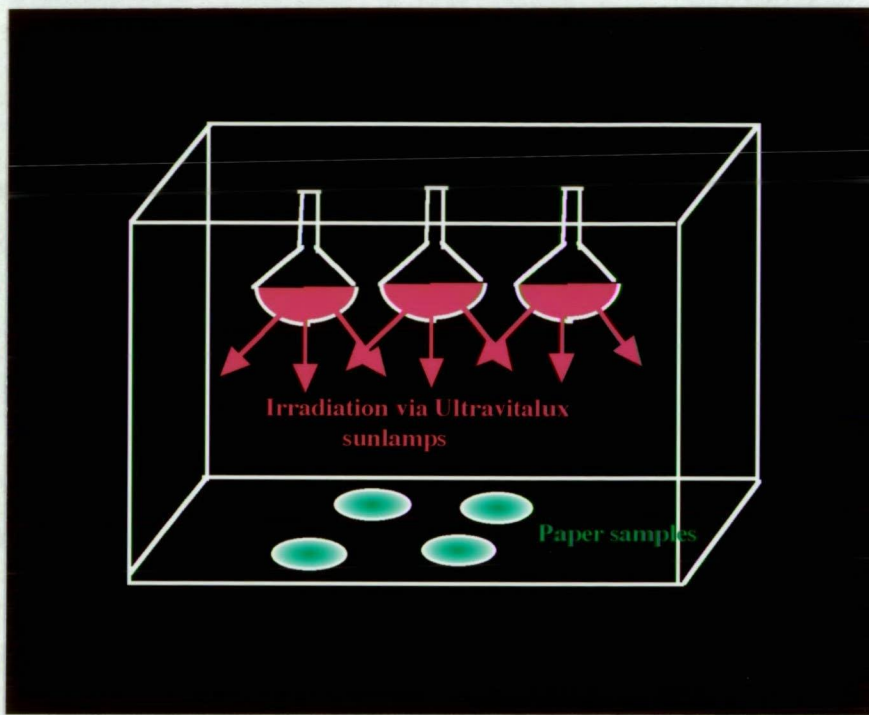
### *Ultravitalux sunlamps*

The Ultravitalux lamps, being mushroom-shaped bulbs, were mounted centrally in series using three lamps (see Figure 2.2). Again a matt black enclosure of dimensions 38 by 99 cm<sup>2</sup> was used, and a wet/dry bulb thermometer was fitted to monitor temperature and relative humidity during irradiations. Due to the heat emitted by these lamps, a small fan was mounted externally, pointing into the chamber through a hole, to provide some ventilation. A tube was also inserted through a hole at the top of the chamber, and then passed into a fume-hood to allow fumes and air to escape.

The uniformity of irradiation in this apparatus was questionable as a result of the bulbous shape of the lamps. Uniformity was thus tested prior to irradiating TMP and BTMP samples by placing 5cm<sup>2</sup> samples of 45.0g/m<sup>2</sup> standard newsprint (PM3, courtesy of ANM Boyer) in a grid formation on the sample shelf. Each square was measured for changes in the tristimulus colour parameters L\*, a\* and b\* after 1 hour of irradiation by the three sunlamps. Due to the low caliper of the standard newsprint, backing sheets were required for these measurements. Samples situated



on opposite sides of the sample shelf were assumed to receive equal irradiation, due to the symmetrical arrangements of the sunlamps. Samples so positioned were therefore used as backing sheets for each other. The results of this are in Section 2.3.1.



**Figure 2.2.** Irradiating chamber containing three Ultravitalux sunlamps.

### 2.2.3 Measuring reversion

#### *a. Testing the photo-reversion ability of each light source*

Photo-reversion ability was monitored by irradiating bleached and unbleached TMP handsheets for five hours and measuring changes in the tristimulus colour parameters  $L^*$ ,  $a^*$  and  $b^*$  hourly using an Elrepho Datacolor 2000 spectrometer. These parameters reveal any colour changes taking place. Four backing sheets were used while taking these measurements.

All irradiations were triplicated and standard deviations accounted for from the averages of measurements and precision of the Elrepho apparatus (calibrated for precision in  $L^*$  less than or equal to 0.02 units).  $a^*$  and  $b^*$  measurements were to one decimal place so it was assumed that precision in these values were no less than 0.1 units.

Dark controls were kept in opaque black plastic bags, in dark drawers at room temperature throughout the experiment.

***b. Comparing the chemical changes induced by each light source***

Chemical changes were compared by taking UV-visible absorption difference spectra of irradiated samples minus their non-irradiated counterparts, using a Varian DMS 100 UV-visible spectrophotometer fitted with an integrating sphere. For each data set a blank (constructed from difference in absorption of an unexposed control sample versus another unexposed control sample) was used as a baseline for all other spectra. For the unbleached versus bleached TMP handsheet difference spectrum, a baseline using white standards was used.

***c. Comparing the spectral energy distributions of each light source***

The spectral energy distributions of each apparatus was measured using an SR9910-PC spectroradiometer with a range of 240-800nm. Measurements of the light sources were taken at night to avoid stray light interference. Three scans, starting as the light source was switched on and taken five minutes apart, were performed to check both the uniformity of irradiation for each apparatus, and to see if a warm-up period was required. SR991-PC Software version 5.0 recorded all plots. Two sun spectra were taken in mid-afternoon, but unfortunately on an overcast day. Therefore, differences may exist between the sun spectra that were recorded, and those which were actually applied to the handsheets on clear, sunny days. These differences would be minor, though, and of little consequence to the *overall general* spectral energy distribution of the sun.

***d. Testing for thermal reversion interference***

Thermal reversion interference was tested by measuring  $L^*$ ,  $a^*$  and  $b^*$  of the unexposed surfaces and comparing the results with those of the exposed surfaces. As with the exposed surfaces, four backing sheets were used in taking these measurements.

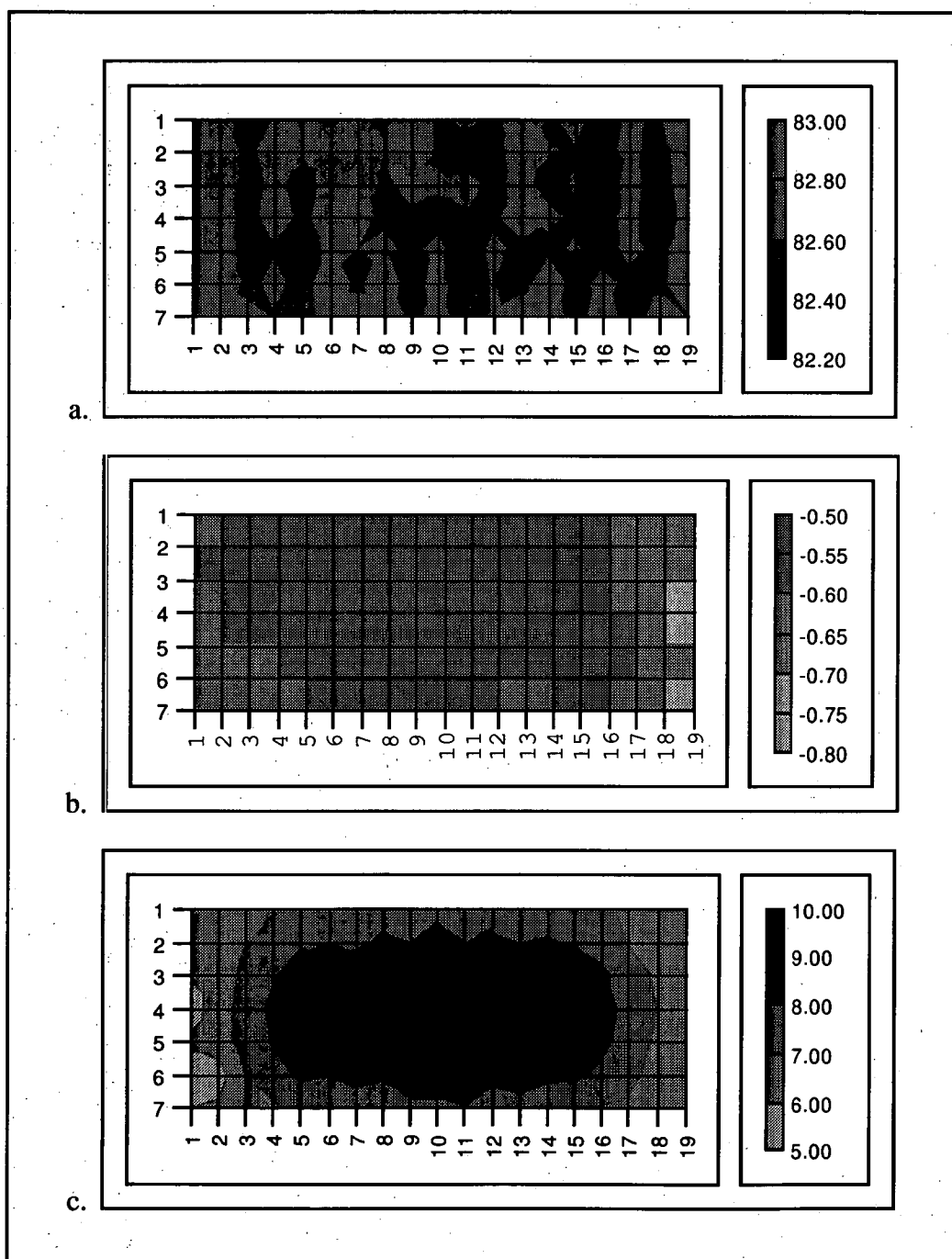
For the thermal reversion check of the Ultravitalux sunlamp, a thick BTMP handsheet of grammage 149g/m<sup>2</sup> was placed under one lamp, which was temporarily mounted on a burette stand approximately 30cm from the sheet. A minimum/maximum thermometer was used to monitor temperature.  $L^*$ ,  $a^*$  and  $b^*$  were measured on both the exposed and unexposed surfaces as above, but for the thicker handsheet no backing sheets were required.



## 2.3 Results and Discussion

### 2.3.1 Uniformity of the Ultravitalux chamber

Figure 2.3 shows the contour plots of the resultant  $L^*$ ,  $a^*$  and  $b^*$  values of standard newsprint after 1 hour of irradiation with the Ultravitalux lamps. The darker shades of grey indicate greater reversion.



**Figure 2.3.** Contour plots of a)  $L^*$ , b)  $a^*$  and c)  $b^*$  for standard newsprint after one hour of irradiation in the reversion chamber containing three Ultravitalux sunlamps.

The temperature in the apparatus rose from  $23\pm1^{\circ}\text{C}$  to  $43\pm3^{\circ}\text{C}$ , and relative humidity dropped from 55% to 20%.

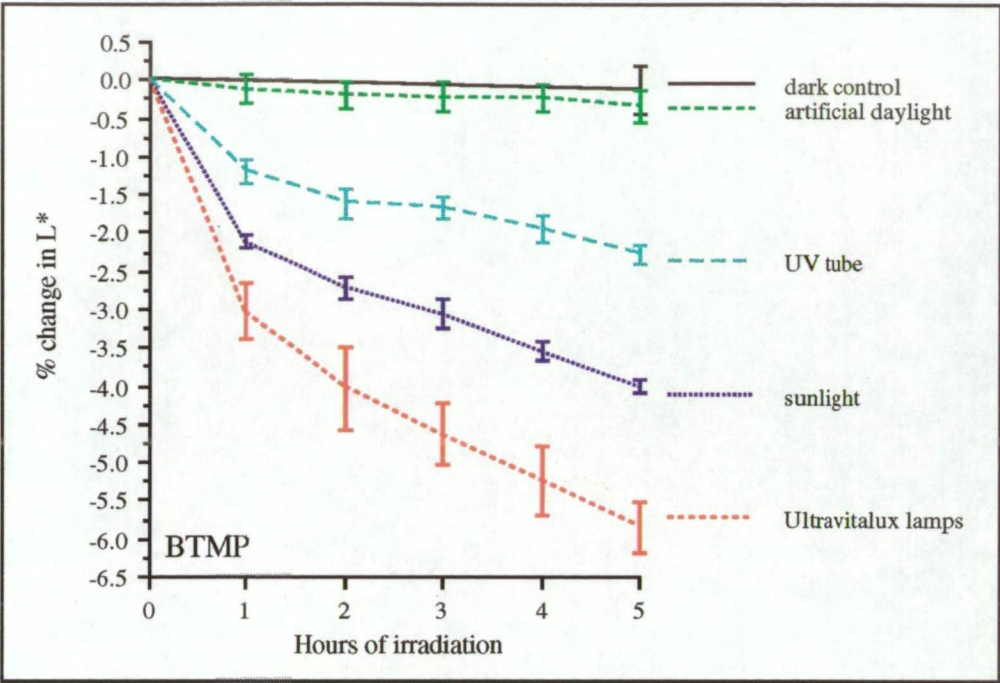
In Figure 2.3a,  $L^*$ , a measure of lightness of surface colouration, with black (value 0) to white (value 100)<sup>2</sup>, revealed a consistent darkening over the whole sample surface, with the majority of the surface fluctuating by only 0.4  $L^*$  units (82.4 - 82.8). The original  $L^*$  values of the samples varied between 83.35 and 83.75.

In Figure 2.3b the  $a^*$  values, originally between -0.8 and -0.9, also revealed a fairly consistent change over the sample surface with final values of -0.5 to -0.6 in the majority of the surface and between -0.6 and -0.7 around the edges. The overall change in  $a^*$  was small, as expected, due to  $a^*$  being a measure of green (negative values) and red (positive values) colouration, while the reversion process is manifested as a yellow discolouration accompanied with darkening. Thus measurements in the red/green regions are generally not sensitive to the chromophores produced during photo-aging<sup>2</sup>.

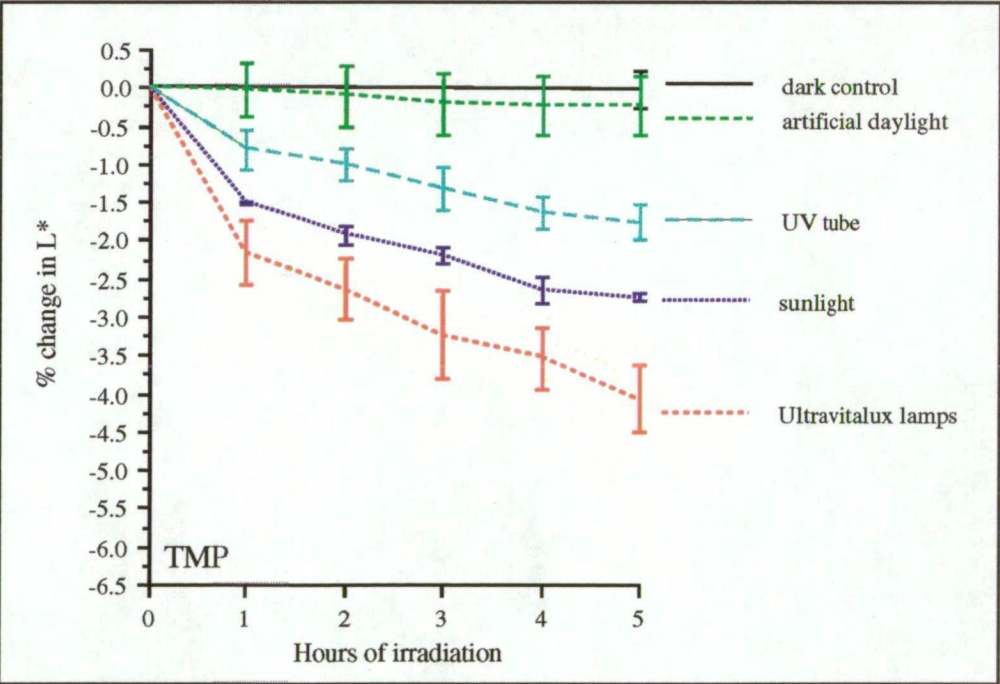
In Figure 2.3c,  $b^*$ , being a measure of blue and yellow colouration (with larger  $b^*$  values depicting greater yellow colouration), produced the most revealing contour plot. Low reversion appeared around the edges, and "hot spots" were revealed directly under the lamps.  $b^*$ , originally between 4.1 and 4.3, increased markedly to values of 6 on the edges and 10 directly under the lamps. Thus these  $b^*$  results were used to map out a sample space under the lamps to produce even discolouration, avoiding the edges and the "hot spots".

### **2.3.2 The ability of each light source to induce photo-reversion on TMP and BTMP handsheets**

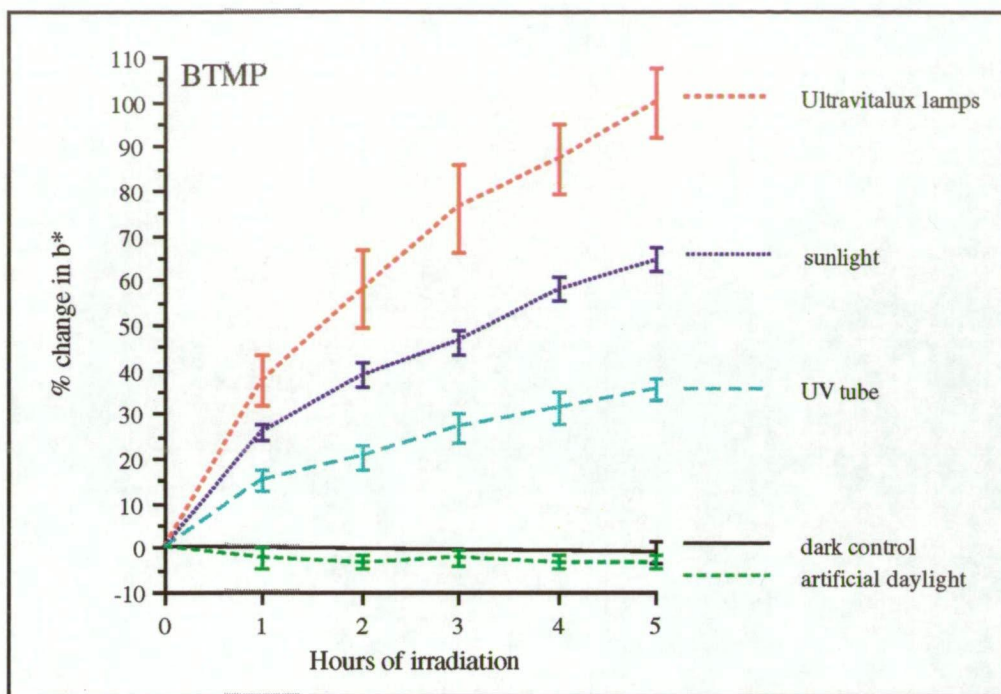
Measurements of  $L^*$ ,  $a^*$  and  $b^*$  for each set of unexposed TMP or BTMP samples naturally revealed similar values. Minor deviations between individual handsheets, however, caused a small spread in the zero exposure data points for each light source. For  $L^*$  and  $b^*$  these deviations were ironed out by calculating changes in the parameters as a percentage difference from their corresponding unexposed value. This normalised each starting point to zero, thus making comparisons easier and, to a small degree, more accurate. Figures 2.4a-d show plots of  $L^*$  and  $b^*$  as percent changes from their original values prior to irradiation against hours of irradiation for both unbleached TMP handsheets (TMP) and peroxide bleached TMP handsheets (BTMP). Each data point represents a mean value of three identically exposed handsheets, and error bars were derived from their standard errors ( $\sigma_{n-1}$ ). Similar plots of  $a^*$  are seen in Figures 2.4e and f, however due to the small values of  $a^*$  percent calculations revealed deceptively high values with large error bars so their direct mean values and standard errors were used.



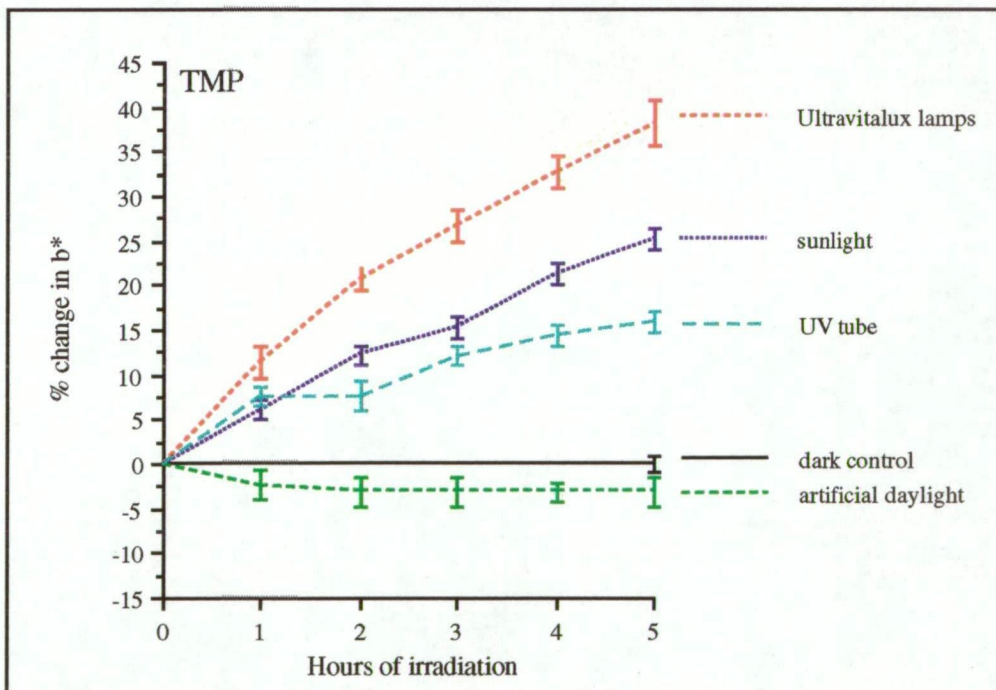
**Figure 2.4a.** Percent changes in L\* from unexposed values against hours of irradiation for bleached TMP handsheets irradiated with each light source.



**Figure 2.4b.** Percent changes in L\* from unexposed values against hours of irradiation for unbleached TMP handsheets irradiated with each light source.

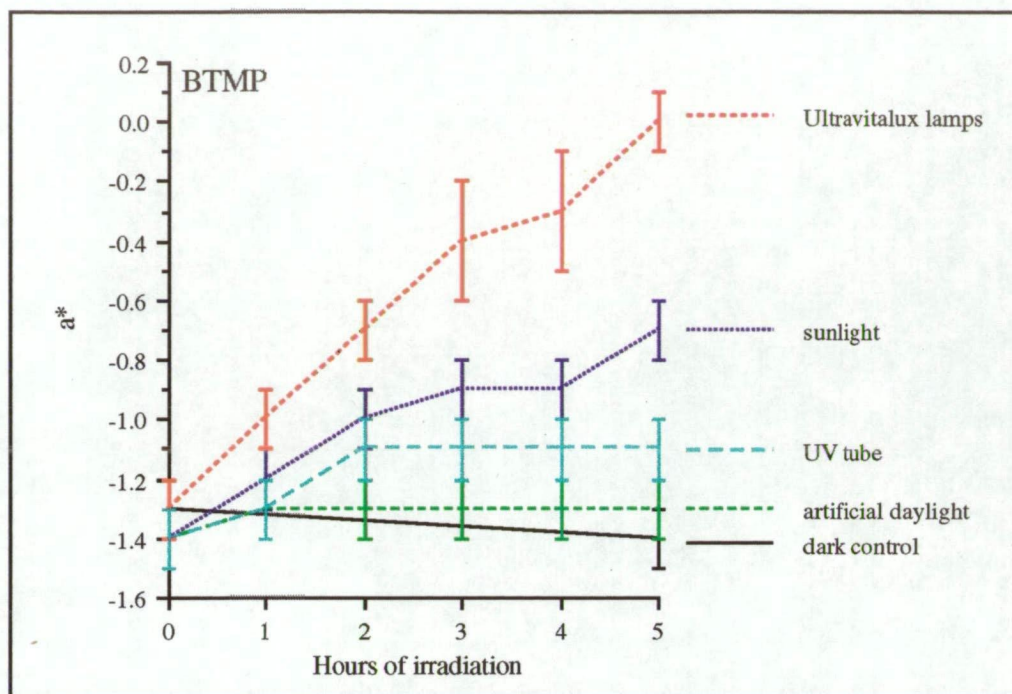


**Figure 2.4c.** Percent changes in  $b^*$  from unexposed values against hours of irradiation for bleached TMP handsheets irradiated with each light source.

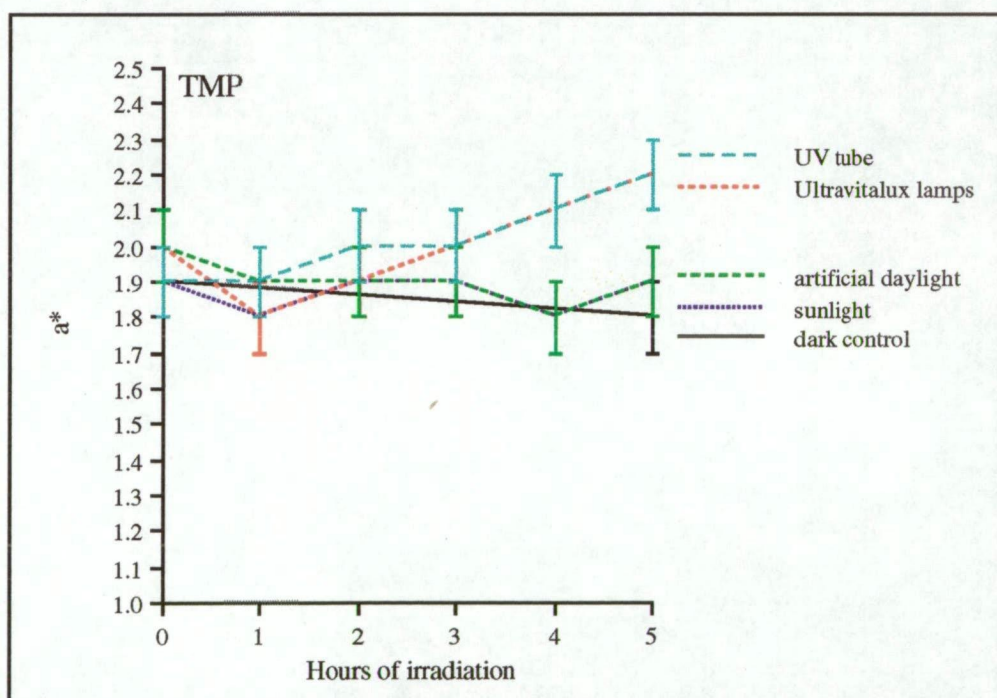


**Figure 2.4d.** Percent changes in  $b^*$  from unexposed values against hours of irradiation for unbleached TMP handsheets irradiated with each light source.





**Figure 2.4e.**  $a^*$  for bleached TMP handsheets irradiated with each light source.



**Figure 2.4f.**  $a^*$  for unbleached TMP handsheets irradiated with each light source.

For both the UV and artificial daylight tubes, no significant temperature rises were observed, with the temperature remaining around  $19 \pm 6^\circ\text{C}$ . For the exposure to the sun, the air temperature ranged between  $17$  and  $28.5^\circ\text{C}$  throughout the exposure periods. For the Ultravitalux lamps, larger temperature increases were observed, with a maximum rise to  $44^\circ\text{C}$ , and average increases of  $12 - 16^\circ\text{C}$ . (Note that initial temperatures for exposure by this source were relatively high, due to a 5 minute warm-up period for all light sources).

For BTMP, in Figure 2.4a,  $L^*$  dropped from an original mean value of 94.08 to 88.58 for the greatest reversion effect (i.e. by the Ultravitalux sunlamps at 5 hours of irradiation). Apart from the artificial daylight tube, a significant drop in  $L^*$  was observed for each light source, including the sun. This indicates that a significant darkening had occurred. The artificial daylight tube may also have caused a slight drop in  $L^*$ , but the result is too close to that of the dark control to be conclusive. The UV tube and Ultravitalux lamps both followed a similar darkening curve to sunlight, with the UV lamp being less effective than the sun, while the Ultravitalux tube was more effective.

In Figure 2.4c,  $b^*$  covered a mean range from 9.3 for unexposed BTMP handsheets up to 18.6 for the greatest yellowing (again, by the Ultravitalux sunlamps at 5 hours of irradiation). Although again being close to the dark control, the artificial daylight tube could possibly have decreased the  $b^*$  value to a small degree. As with the questionable but possible drop in  $L^*$ , this small decrease in  $b^*$  could be due to a minor photo-bleaching effect, but again this change was too small to be conclusive. The remaining light sources have clearly increased the yellowness of the handsheets. The relative extents of yellowing observed for each light source was the same as the relative extents for the darkening, or decreases in  $L^*$ , discussed above. That is, the Ultravitalux lamps afforded the greatest extent of yellowing, followed by natural sunlight, and then the UV tube.

In Figure 2.4e,  $a^*$  ranged from -1.4 for the unexposed samples up to 0.0 for samples exposed to the Ultravitalux sunlamps, suggesting a slight change in hue towards a reddish colour<sup>2,9</sup>. Andrady et al.<sup>9</sup> also revealed a change in hue towards red for yellowed TMP exposed to wavelengths less than 400nm. For exposure to wavelengths greater than 400nm, however, they found a slight change in hue towards green (-ve). The artificial daylight tube did not veer toward red. This is further evidence of the absence of photo-yellowing by this light source. It is still unclear, however, whether any photo-bleaching had occurred, as there was also no clear change in hue towards green. For each other light source, the values of  $a^*$  were small, and not greatly significant to photo-reversion. The large error bars also make any trends less definable than for the  $L^*$  and  $b^*$  parameters, however if any trends are to be interpreted, they appear to be similar to those observed with the  $b^*$  plots.

For TMP,  $L^*$  (Figure 2.4b) ranged from 89.79 for the unexposed sample down to 86.14 for the greatest darkening observed.  $b^*$  (Figure 2.4d) ranged from an original mean value of 13.1 up to 18.1 for the greatest yellowing effect.  $a^*$  (Figure 2.4f) increased from an original value of 1.9 to 2.2. In each case the reversion trends were similar to the BTMP results discussed above, only much less intense. There could be two possibilities for this;



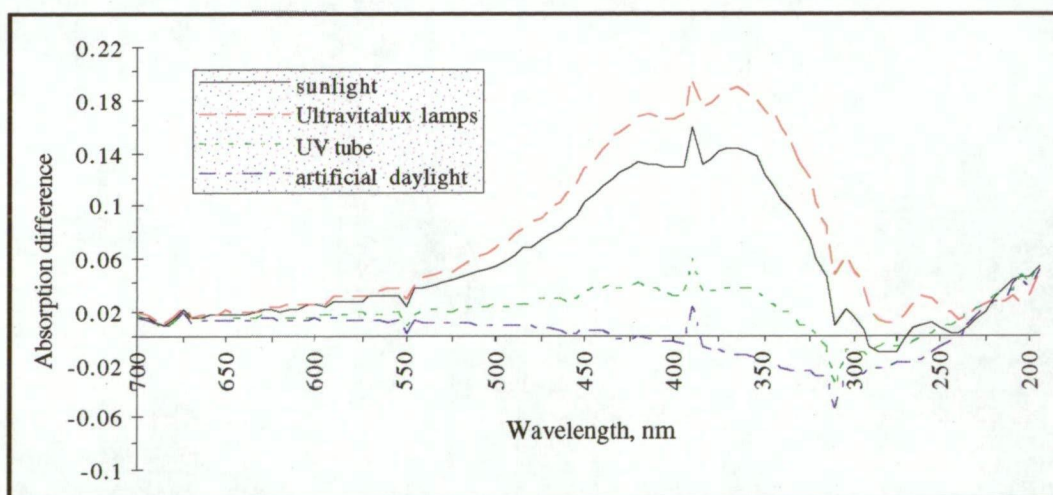
a. Either BTMP has undergone greater photo-reversion than TMP, with more chromophores produced, or

b. TMP and BTMP could both have undergone a similar extent of photo-reversion, with similar extent of chromophore production. The higher values for BTMP could be a result of its original higher brightness and whiteness. Even a small increase in colour producing chromophores could manifest as  $L^*$  and  $b^*$  values greater than those of the originally darker TMP handsheets, even if chromophore production levels were the same.

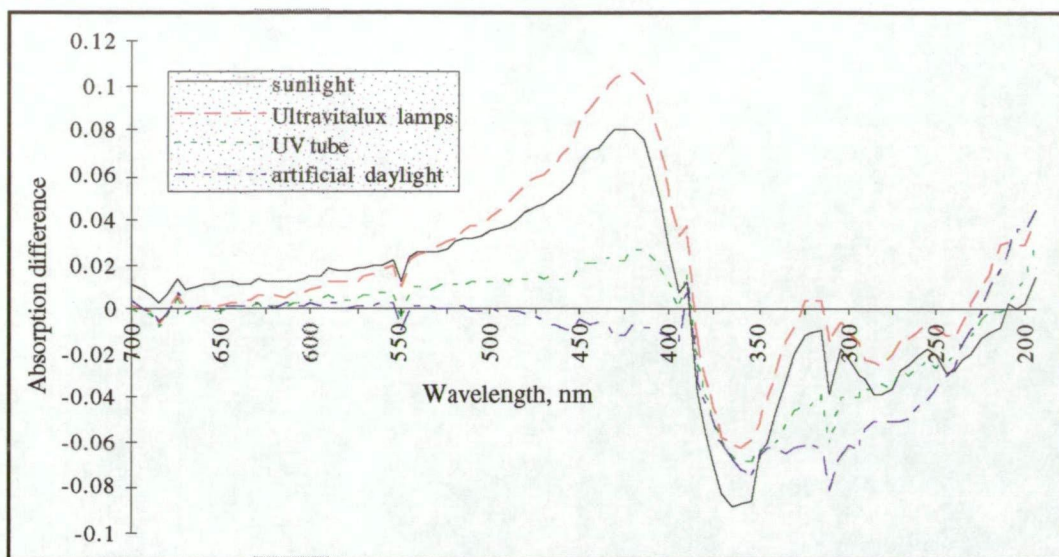
An indication of which of these possibilities had occurred could be gained by measuring and comparing the absorption coefficients  $k$ , which are directly proportional to the amount of chromophores absorbing at a given wavelength (see Section 1.4). Such measurements were carried out for Chapter 3, where comparisons between TMP and BTMP are more important. For the purpose of this chapter, however, it is the relative differences between each light source which is of primary concern.

### 2.3.3 Comparison of chemical changes induced by each light source

UV-visible absorption difference spectra were taken for each exposed sample against a dark control reference. These spectra are shown in Figures 2.5a and b.

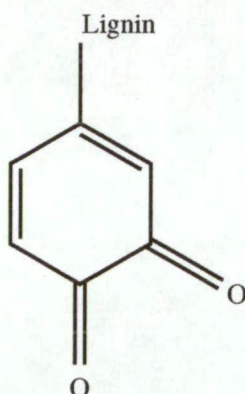


**Figure 2.5a.** UV-visible absorption difference spectra of bleached TMP handsheets irradiated for five hours by each light source, against unexposed controls.



**Figure 2.5b.** UV-visible absorption difference spectra of unbleached TMP handsheets irradiated for five hours by each light source, against unexposed controls.

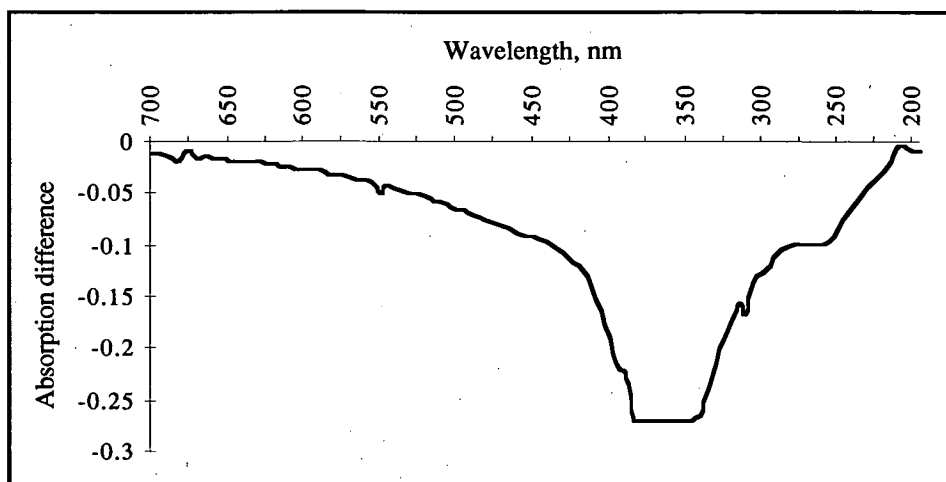
The difference spectra in Figures 2.5a and b reveal increases in absorption around 430nm for both TMP and BTMP exposed to each light source, except the artificial daylight tube. This absorption peak is commonly referred to as the “yellowing” peak and results from the formation of *ortho*-quinones<sup>10</sup> (see below), which absorb at this wavelength.



Ortho-quinone structure.

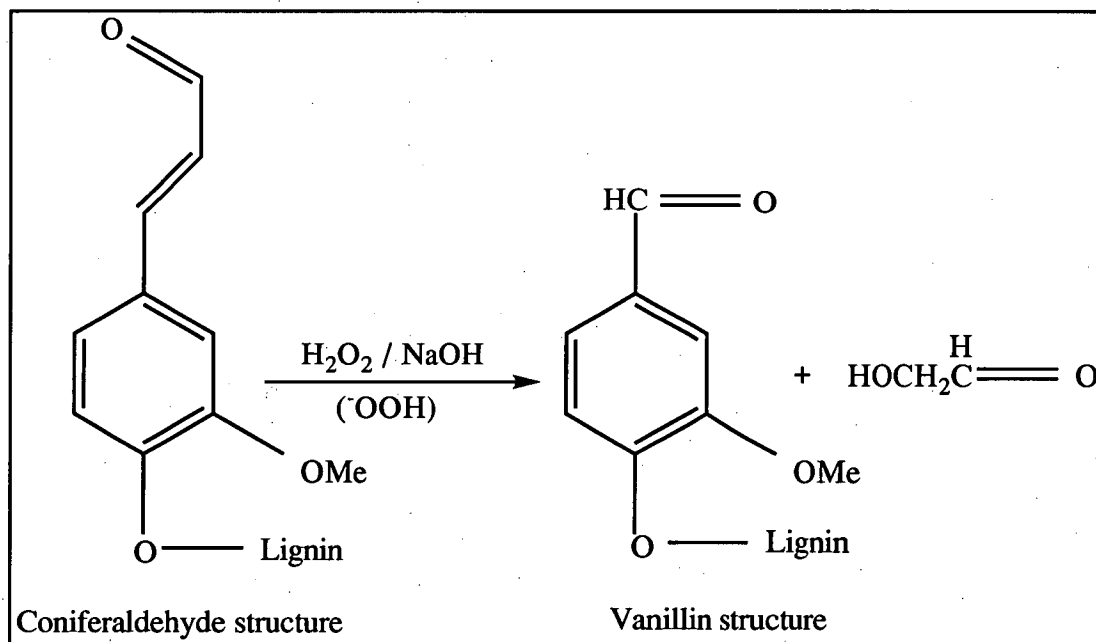
In the 360nm region of the spectra, however, there is an obvious difference in the responses to irradiation between TMP and BTMP. While the reversion curves of TMP contain a large dip in this region (Figure 2.5b), the BTMP curves do not (Figure 2.5a). Coniferaldehyde structures absorb in this region<sup>10</sup>, suggesting a depletion of these species during photo-reversion of TMP, but not BTMP. This is simply due to BTMP lacking these species to begin with. A UV-visible absorption difference spectrum of *non-irradiated* TMP versus BTMP (Figure 2.6), reveals a large dip in this same region, suggesting that the alkaline peroxide bleaching process removes these structures.





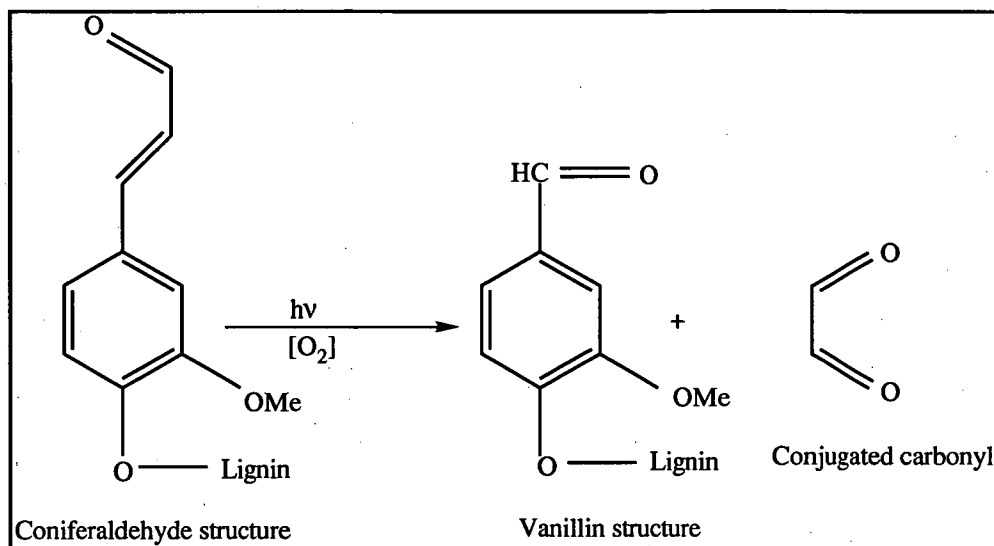
**Figure 2.6.** UV-visible absorption difference spectra of bleached TMP handsheets against unbleached TMP handsheets.

This is likely to be due to a cleavage of the C=C bond in the coniferaldehyde group of lignin by the peroxide, as shown in Reaction 1 below.



**Reaction 1.** Removal of coniferaldehyde structures in lignin with alkaline hydrogen peroxide bleaching<sup>41</sup>.

In TMP, coniferaldehyde structures are possibly removed by photo-oxidative cleavage in the presence of UV radiation and oxygen, to form conjugated carbonyls (particularly ketones). These absorb around 300-330nm<sup>41</sup>, which is consistent with the appearance of a peak in this region of the spectra. This process is shown in Reaction 2 below.



**Reaction 2.** Photo-oxidative cleavage of coniferaldehyde structures into conjugated carbonyls, induced by UV radiation<sup>41</sup>.

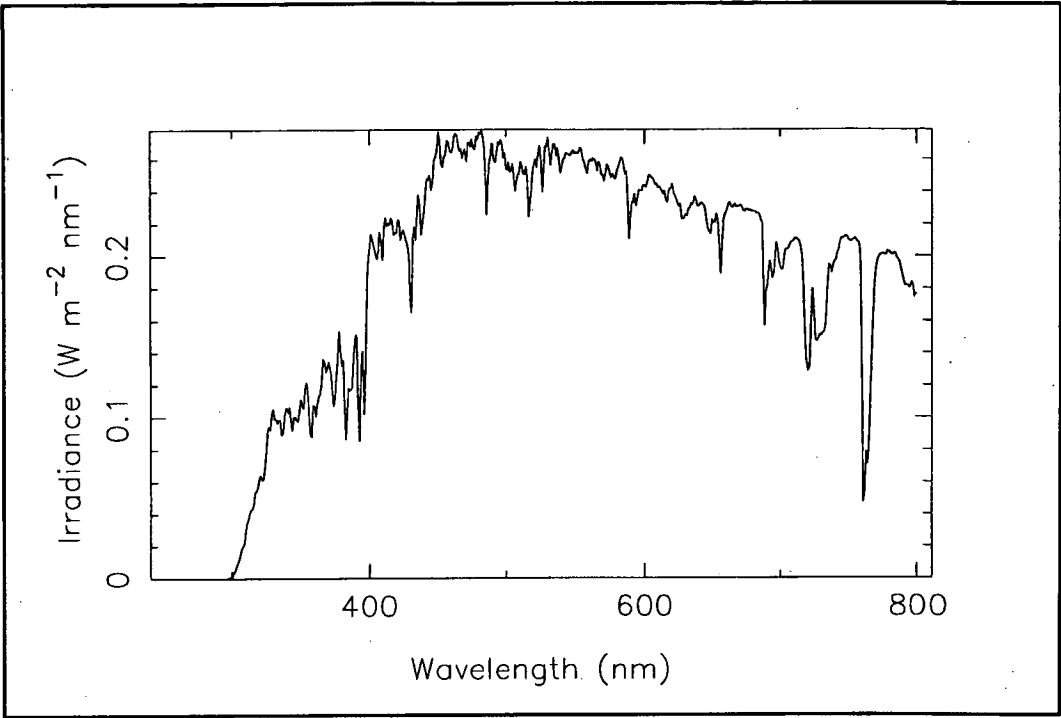
The sharp peak at 400nm in the irradiated BTMP spectra (see Figure 2.5a) was not a result of absorption by chemical species within the handsheet. It was instead an anomaly caused by a change in light source at this point within the spectrophotometer. The presence of this peak makes it uncertain if there is one large peak due to *o*-quinone production, or if a shouldering peak has also formed next to it around 370nm. The absorption in this spectrum is also very broad, masking other spectral regions which may or may not have undergone changes. Thus it is unclear from these spectra whether or not BTMP has actually undergone different or more intense reversion than TMP. So it is still uncertain whether the greater changes in *L*\* and *b*\* observed for irradiated BTMP were due to a greater extent of reversion, or merely to a higher sensitivity to changes in these parameters.

In both Figures 2.5a and 2.5b, for TMP and BTMP, the Ultravitalux lamp has induced a curve very closely matched to those induced by the sun. Thus it appears to be following a chemical route similar to natural sunlight with respect to photo-reversion. The UV tube seems also to be similar, only much less intense. The difference spectra for the samples irradiated with the UV tube may be lacking some absorption between 330 and 220nm, but this is uncertain, as very small peaks may exist. Thus, although the UV tube induced similar UV-visible absorption spectra to those shaped by sun, the Ultravitalux lamp induced a closer match, proving to be more representative of natural photo-reversion induction.

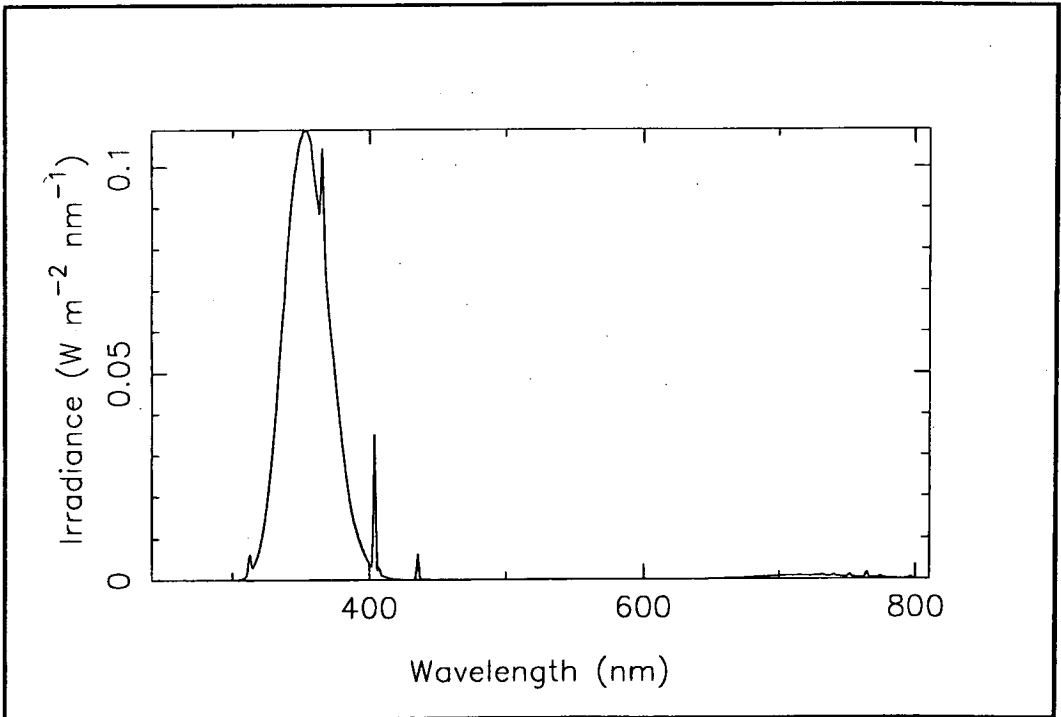
The artificial daylight tube has shown virtually no chemical changes with respect to the unexposed controls (blanks). It is certainly not representative of natural sun induced reversion, and if any photo-bleaching has occurred, it is too weak to be detected here.

**2.3.4 Spectral energy distributions of each light source**

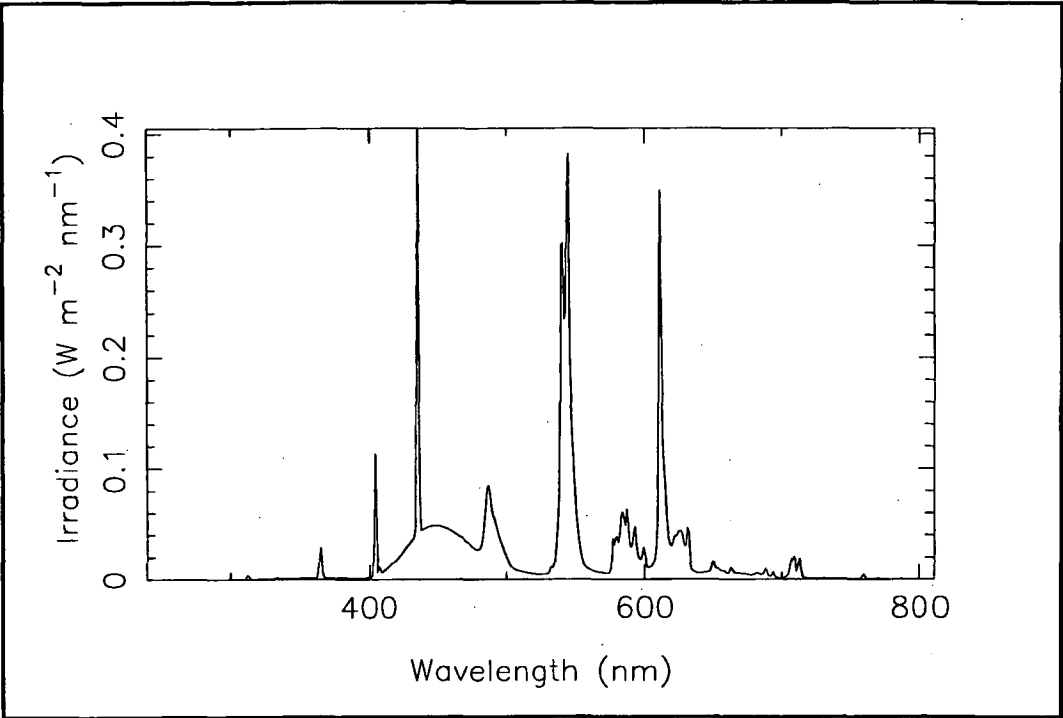
Spectral energy distributions of each light source and the sun are shown in Figures 2.7a - d.



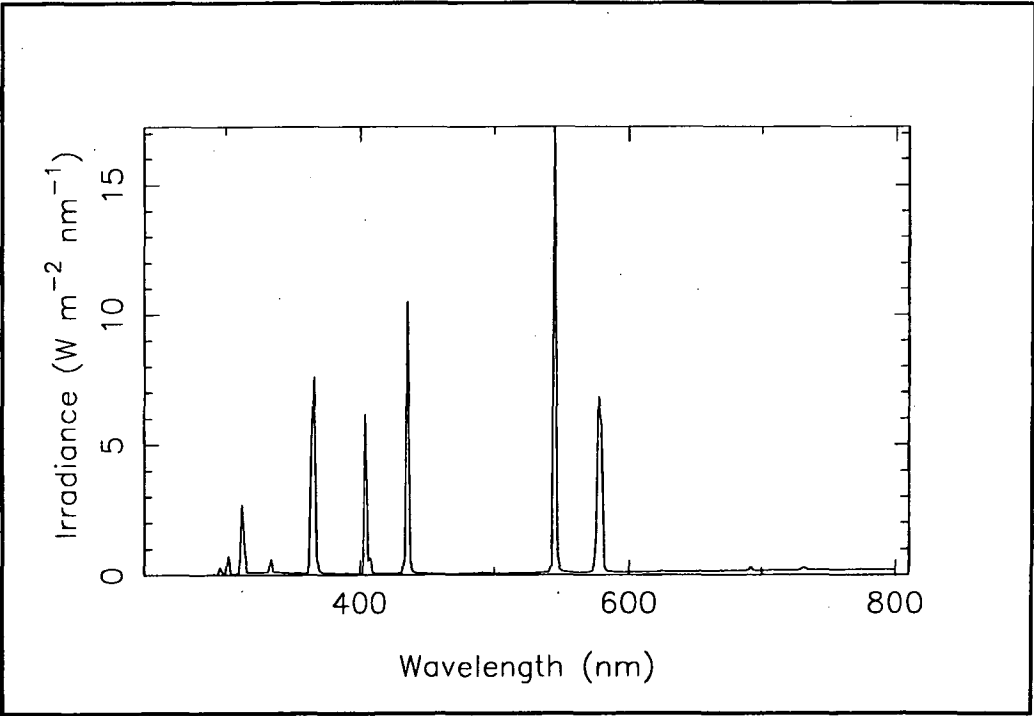
**Figure 2.7a.** The spectral energy distribution of sunlight.



**Figure 2.7b.** The spectral energy distribution of the UV blacklight tube.



**Figure 2.7c.** The spectral energy distribution of the artificial daylight tube.



**Figure 2.7d.** The spectral energy distribution of the Ultravitalux sunlamps.

The sun (Figure 2.7a) revealed a broad spectrum, with its UV component about half as intense as the 400-600nm region.

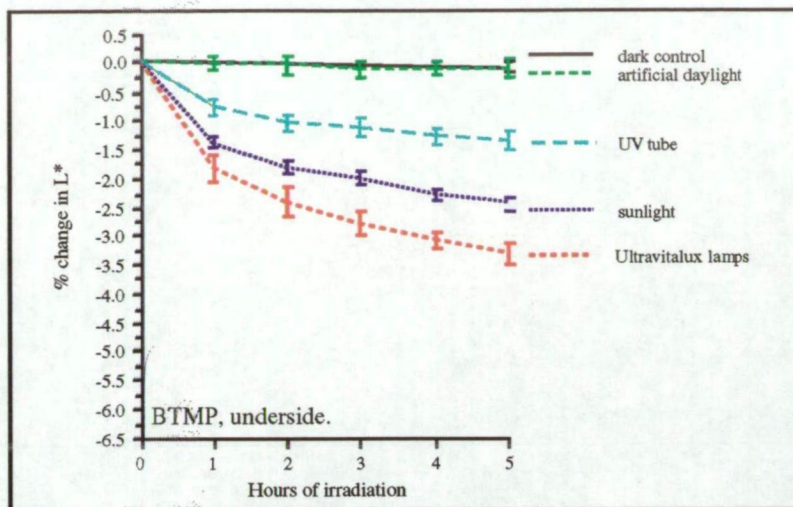
The UV tube (Figure 2.7b), as expected, exhibited only one peak at 360nm. This confirms the significant role UV radiation plays in the photo-reversion of lignin-rich papers, as it yellowed both TMP and BTMP significantly.

The artificial daylight tube seemed severely compromised in its UV region, unable as it was to photo-revert the TMP and BTMP handsheets. Its spectral energy distribution (Figure 2.7c) revealed that it was in fact deficient in the UV region, with only the higher wavelength visible region present.

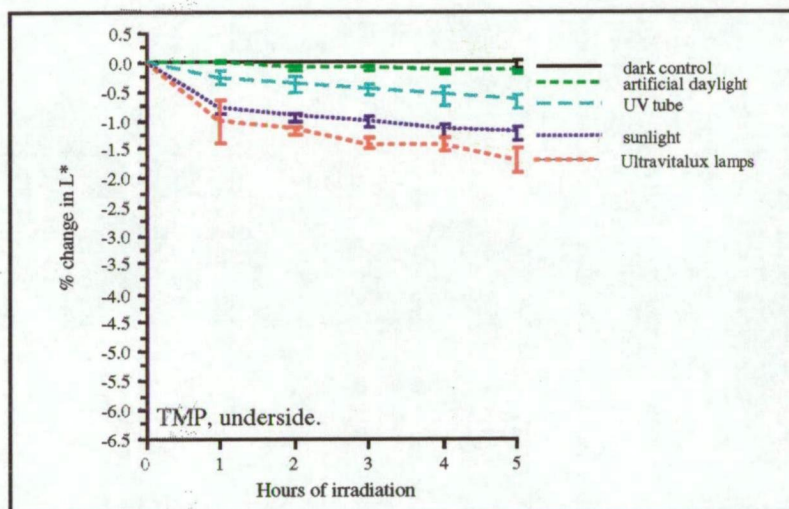
The spectral energy distribution of the Ultravitalux sunlamp (Figure 2.7d) was not as broad as that of sunlight (Figure 2.7a). It did, however, contain both strong UV components and 400-600nm peaks, with the latter region being more intense, in accordance with the spectral proportions revealed for sunlight. As these are the most significant spectral regions with regards to photo-reactions of lignin-rich pulp and paper, the Ultravitalux lamp appears to be a good model of natural sunlight for paper reversion studies. Of the three scans taken of this light source, the final two were identical. The first scan had a few minor differences from these, indicating that a warm up of the lamp, (about 5 minutes), is required for irradiation experiments. For both the artificial daylight and UV tubes, each of the three spectra taken were identical. A warm-up period prior to irradiations with these lamps is thus not required.

### **2.3.5 Tests for thermal reversion interference**

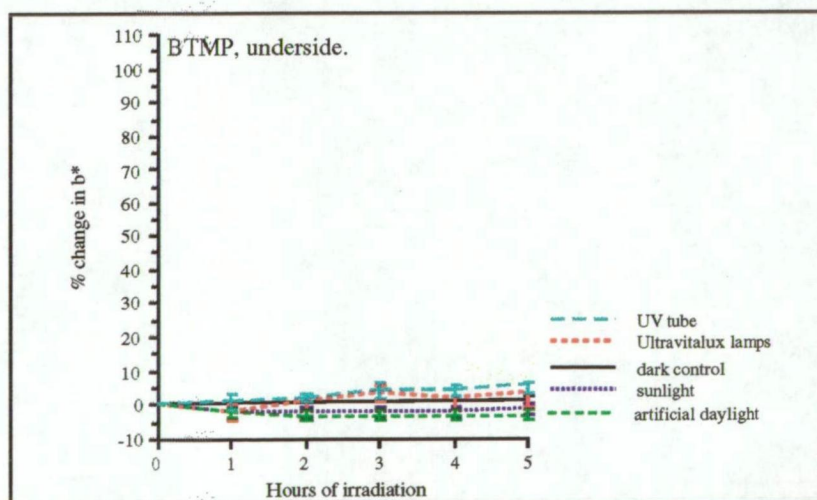
Figures 2.8a - f show plots of  $L^*$ ,  $a^*$  and  $b^*$  constructed as with Figures 2.4a - f, but for the unexposed surfaces of each set of handsheets. (Note that these figures are drawn to the same scale as Figures 2.4a - f, so that comparisons between the exposed and unexposed surfaces can be easily observed).



**Figure 2.8a.** Percent changes in  $L^*$  from unexposed values against hours of irradiation for the unexposed surfaces of bleached TMP handsheets irradiated with each light source.

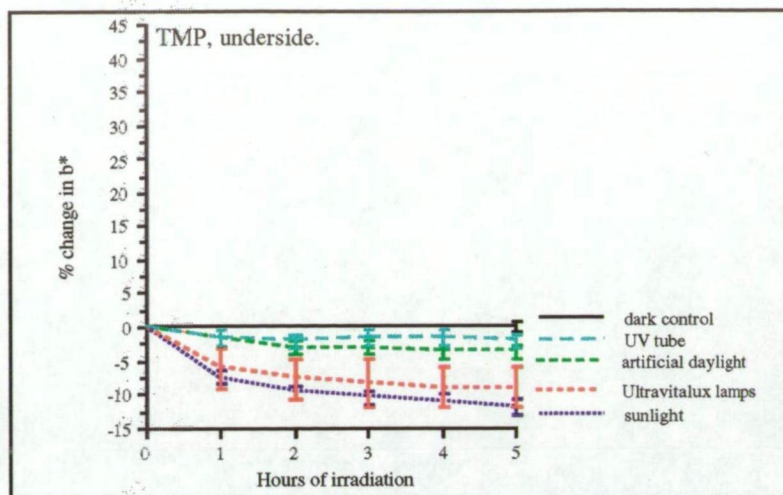


**Figure 2.8b.** Percent changes in  $L^*$  from unexposed values against hours of irradiation for the unexposed surfaces of unbleached TMP handsheets irradiated with each light source.

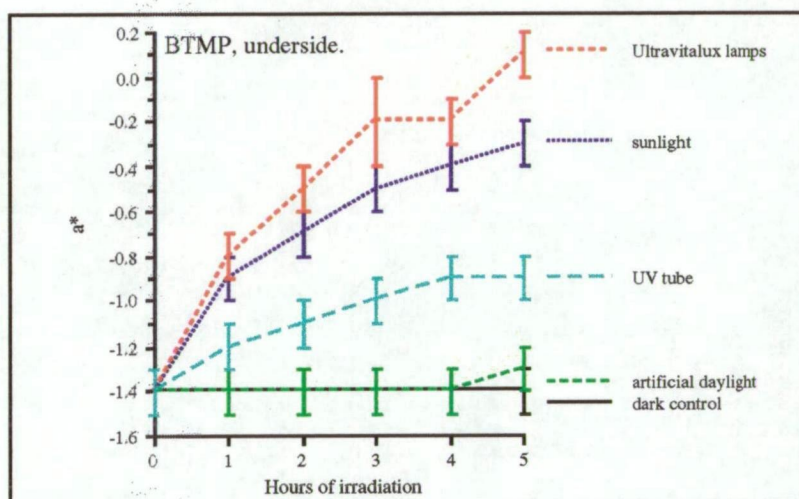


**Figure 2.8c.** Percent changes in  $b^*$  from unexposed values against hours of irradiation for the unexposed surfaces of bleached TMP handsheets irradiated with each light source.

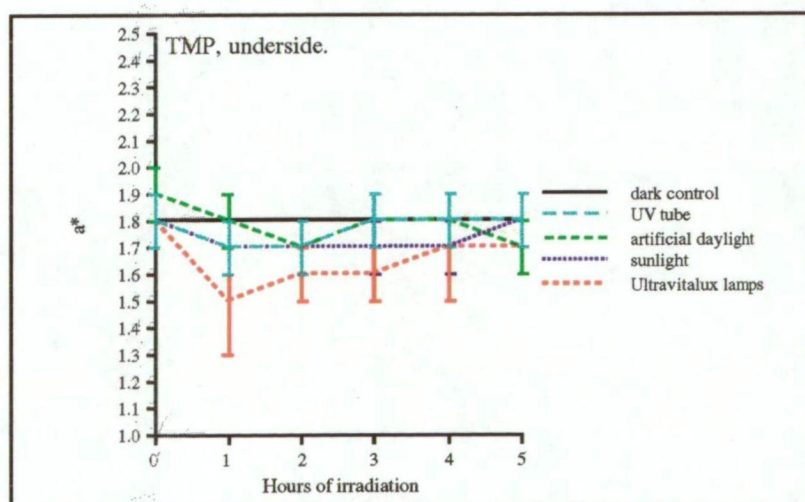




**Figure 2.8d.** Percent changes  $b^*$  from unexposed values against hours of irradiation for the unexposed surfaces of unbleached TMP handsheets irradiated with each light source.



**Figure 2.8e.**  $a^*$  for the unexposed surfaces of bleached TMP handsheets irradiated with each light source.



**Figure 2.8f.**  $a^*$  for the unexposed surfaces of unbleached TMP handsheets irradiated with each light source.

For  $a^*$  (Figures 2.8e and f) the results are similar in both trend and magnitude to the corresponding exposed surfaces (Figures 2.4e and f). Thus, in general, changes in hue could be a result of photo-bleaching and/or thermal reversion as both of these effects are penetrating.

For  $b^*$  of BTMP (Figure 2.8c) changes were negligible within error, suggesting negligible thermal reversion or photo-bleaching. For TMP (Figure 2.8d), however, there may have been a very slight yellowing, and therefore thermal reversion, in the cases of the sun and Ultravitalux lamps.

For  $L^*$ , (Figures 2.8a and b) significant drops were revealed in both BTMP and TMP, similar to those for the exposed surfaces, but about halved in intensity. This could, however, be due merely to the darkening observed on the irradiated surfaces showing through, affecting the  $L^*$  values of these unexposed surfaces. It can be assumed that this is indeed the case for the UV tube, as it lacks photo-bleaching spectral regions, and did not emit heat during irradiation, so thermal reversion could not have occurred. Also natural thermal reversion (i.e. at room temperature) could not have occurred in such a short time frame, as is confirmed by the lack of darkening seen by the dark control. To check this, a comparison of the ratio of  $UV_{\text{exposed}}:UV_{\text{unexposed}}$  surfaces to similar ratios for the sun and Ultravitalux exposed samples was made. If the ratios of the latter samples were similar to that of the UV exposed sample, then it could be assumed that the darkening observed on the underside was merely a manifestation of the colouration in the exposed surfaces showing through. If ratios were lower, however, then it would be probable that thermal reversion had occurred. These ratios are shown in Table 2.1.

**Table 2.1.** Ratios of  $L^*$  for surfaces of handsheets exposed to 5 hours of irradiation to their corresponding unexposed surfaces.

	UV tube 5hrs : 0hrs	sunlight 5hrs : 0hrs	Ultravitalux lamps 5hrs : 0hrs
BTMP	91.91:93.27 = 0.99	90.49:92.31 = 0.98	88.58:91.41 = 0.97
TMP	88.44:89.48 = 0.99	87.61:88.99 = 0.98	86.14:88.50 = 0.97

As these ratios are all similar, it is unlikely that thermal reversion has occurred. In the case of the Ultravitalux lamps, however, this was double checked using thicker BTMP handsheets ( $149 \text{ g/m}^2$ ) which were exposed to the Ultravitalux lamps for 2 hours. The temperature rose to  $56^\circ\text{C}$ . Results of  $L^*$ ,  $a^*$  and  $b^*$  for both the exposed surfaces and unexposed surfaces are shown in Table 2.2.



**Table 2.2.** L\*, a\* and b\* for both the exposed and unexposed surfaces of a thick bleached TMP handsheet exposed to irradiation from the Ultravitalux lamps for 2 hours.

	L*	a*	b*
Initial value, exposed surface.	93.42	-1.0	10.7
Initial value, unexposed surface.	93.55	-1.1	11.1
2 hrs irradiated, exposed surface.	89.34	0.0	16.8
2 hrs irradiated, unexposed surface.	93.29	-1.1	10.4
$\Delta(2\text{hrs} - \text{initial value})$ , exposed surface.	-4.08	+1.0	+6.1
$\Delta(2\text{hrs} - \text{initial value})$ , unexposed surface.	-0.26	0.0	-0.7

From this table, it is evident that the unexposed surface of the thick bleached TMP handsheet has undergone insignificant discolouration/darkening compared to the exposed surface. Thus thermal reversion complications can be assumed to be negligible.

## 2.4 Conclusions

- For the purpose of photo-reversion studies of paper UV tubes were found to match natural reversion quite well, but the Ultravitalux lamp was a better match.
- The Ultravitalux lamp was found to contain both photo-yellowing and photo-bleaching spectral regions in proportion to those of sunlight.
- Irradiation experiments on peroxide bleached and unbleached TMP handsheets revealed a predominant yellowing effect by the Ultravitalux lamp, as was also the case for natural sunlight. Although these lamps emitted high temperatures thermal reversion complications were found to be negligible.
- The chemical routes of the reversion under the Ultravitalux lamp appeared to match those of reversion under natural sunlight, as evidenced by measurement of UV-visible difference absorption spectra.
- Finally it should be noted that the effect on the paper of the artificial daylight tube studied did not resemble natural photo-reversion at all, nor did its spectral components represent sunlight adequately for pulp and

paper reversion purposes. Thus one should be careful when choosing "off the shelf" "artificial daylight / sunlight" sources.

The Ultravitalux sunlamps were therefore chosen as the artificial photo-reversion induction source throughout the remainder of this thesis. The set up of these lamps exhibited "hot spots" directly under the lamps, and these areas were avoided in subsequent irradiation experiments, to ensure consistent reversion of all samples. The chamber was also duplicated so untreated controls could be irradiated separately to chemically-treated samples. This avoided possible cross-contamination by vapours in subsequent experiments.

## CHAPTER 3

# INHIBITION OF THE LIGHT-INDUCED REVERSION OF TMP AND BTMP HANDSHEETS USING MERCAPTANS

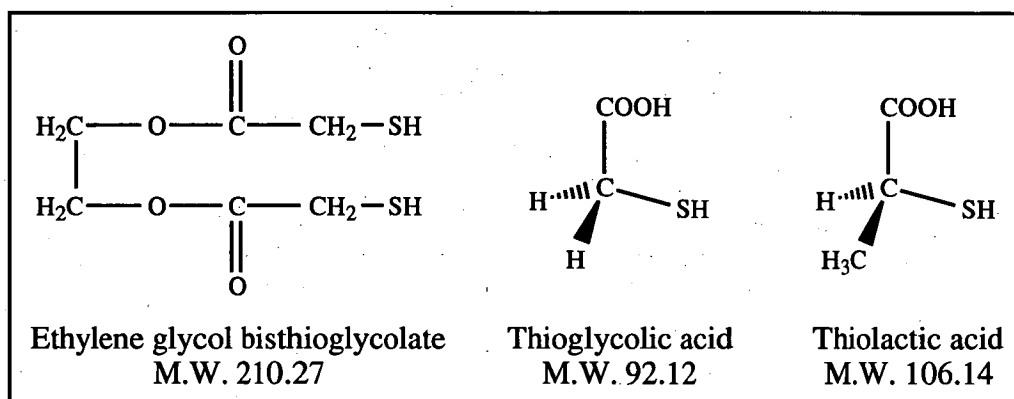
### 3.1 Inhibition of the Light-Induced Reversion of TMP and BTMP Handsheets by EGB, Thg and Thl

#### 3.1.1 Introduction

Section 1.3 introduced several potential ways to inhibit the photo-induced reversion of lignin-rich pulps and papers. Mercaptans were highlighted due to the theoretical possibility of these compounds to target several steps in the photo-reversion process. For example they can act as reducing agents<sup>111</sup> during the oxidative reversion processes. They are also good hydrogen donors<sup>97</sup> and therefore theoretically able to replace H-atoms after their photo-induced abstraction, hindering one of the key steps in photo-reversion (see Section 1.2). Being good radical scavengers<sup>97</sup> they could also deactivate radicals formed by irradiation and thus prevent their subsequent formation into coloured products or their initiation of further H-abstraction steps. Degradation products of some mercaptans could also hinder photo-reversion by acting as antioxidants<sup>111</sup>. Several mechanisms for the inhibitory action of mercaptans have been suggested, and were discussed in Section 1.3. These included the addition of the mercaptan compounds to yellow precursors, preventing their further reaction<sup>97</sup>; addition to yellow products as they form, and thus effectively removing them<sup>97</sup>; and steric hindrance or “blocking” of photo-active sites<sup>98</sup>. The rest of this thesis will investigate the inhibition of photo-induced reversion by mercaptans, and explore some of the above-mentioned mechanistic proposals along with others.

This chapter introduces three mercaptans and gauges their activity on TMP and peroxide bleached TMP (BTMP) handsheets. The three mercaptans selected were kept relatively simple. Ethylene glycol bithioglycolate (EGB) is a mercaptan containing two carbonyl groups and two thiol end groups. Thioglycolic acid (Thg) and Thiolactic acid (Thl) both contain one thiol end group and one carboxylic acid group, with Thl also containing one methyl group. EGB and Thg have both been

shown to inhibit reversion quite well (see Section 1.3) but their modes of action are not fully understood. The structures of these compounds are shown below:



### 3.1.2 Experimental procedures

TMP and BTMP handsheets were made following the procedures previously described in Chapter 2. They were then soaked in solutions of mercaptans in acetone for 5 minutes and left to air dry. After drying, one set of samples was subsequently washed thoroughly with acetone, and then air-dried again (referred to as “washed” samples). This washing procedure was included to gauge whether it was necessary for the mercaptans to remain within the handsheet during irradiation for inhibition to occur. The load of each mercaptan absorbed into the handsheets was calculated as the percent increase in the mass of the handsheet after drying. Treatment of samples with acetone alone resulted in no increase in mass for any samples, indicating that this solvent underwent complete evaporation on drying. Therefore, for the mercaptan treated samples, any increase in mass was attributed to absorbed mercaptan only.

Controls included untreated samples and solvent (acetone) samples. Dark controls were also included, and were stored under the same conditions as previously described in Chapter 2. As these dark controls did not differ significantly from the results already presented in Chapter 2, with insignificant colour changes recorded for both untreated and treated samples, they will not be discussed further.

Samples were subjected to three hours of irradiation in the irradiation chamber containing Ultravitalux sunlamps, introduced in Chapter 2. To monitor the extent of colouration caused by each irradiation, the tristimulus colour parameters  $L^*$ ,  $a^*$  and  $b^*$  were measured by the same procedures described in Chapter 2.

### 3.1.3 Results and discussion

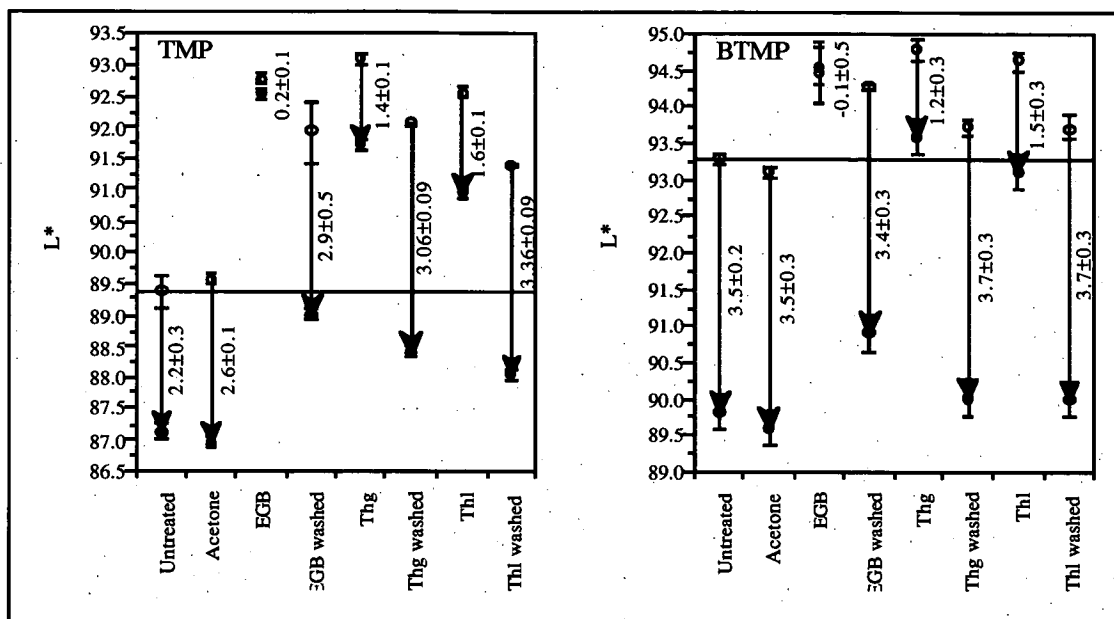
The percent loads of each mercaptan absorbed into the handsheets are shown in Table 3.1.

**Table 3.1.** Loads of mercaptans absorbed by TMP and BTMP handsheets, based on the percentage increases in mass after treatment and subsequent drying.

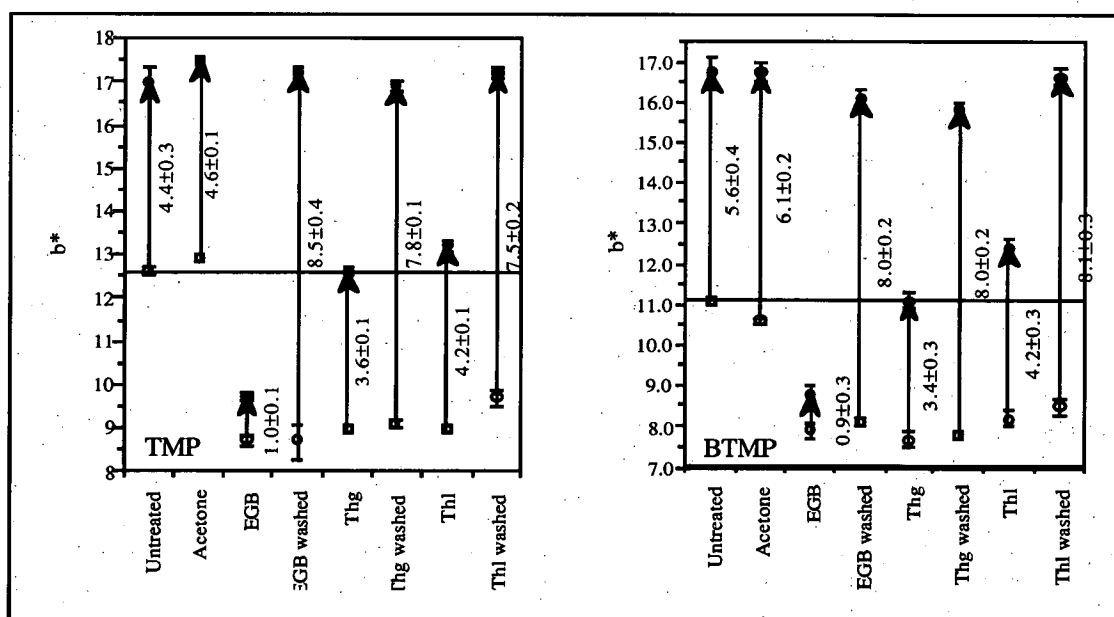
treatment	% load, TMP	% load, BTMP
acetone control	-1.0±0.2	-1.1±0.3
EGB	15.7±0.4	14.0±0.9
EGB washed	2.5±0.4	1.6±0.1
Thg	11.7±0.3	10.8±0.5
Thg washed	1.1±0.1	1.2±0.1
Thl	11.9±0.3	11.8±0.6
Thl washed	0.6±0.1	0.8±0.3

It appears that EGB absorbs into the handsheets more efficiently than the other mercaptans. This could be due to the higher molecular weight of EGB compared to the other two mercaptans resulting in a greater mass of samples treated with EGB. Alternatively it could be due to a higher reactivity of the EGB towards components in the handsheets. For example EGB has twice the number of -SH end groups (and C=O groups) per molecule than the other mercaptans. If Michael-type additions of the -SH end groups and lignin constituents occur, like those proposed by Cole et al.<sup>97</sup> and reproduced in Section 1.3, then perhaps this could account for a greater activity of EGB over the other mercaptans. On the other hand, EGB, being more viscous than the other mercaptans may just adhere to the handsheets more efficiently. Removal of the mercaptans, by washing the samples with acetone, was almost complete in each case, but more so for Thg and Thl. So whether the reason for EGBs greater percent load was due to its molecular weight, chemical reactivity, or physical adsorption being greater, it was harder to remove than the other two mercaptans.

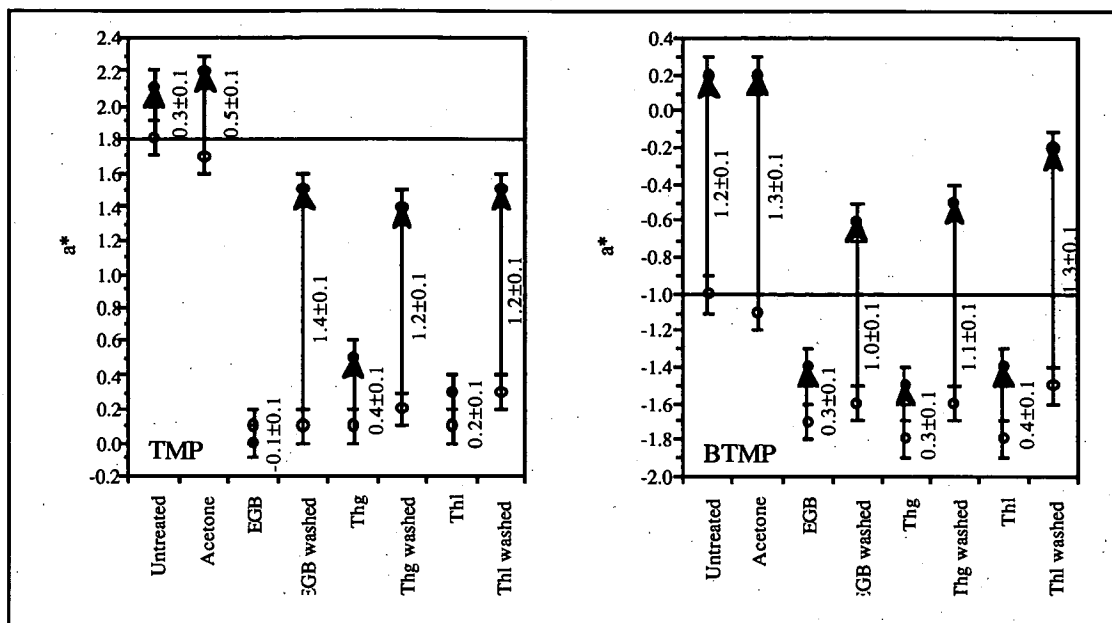
The results of irradiating each sample are shown in Figures 3.1a, b and c for both TMP (left) and BTMP (right). Each plot reveals the colour parameter for each sample prior to irradiation, after irradiation, and the magnitude of the changes in each colour parameter by irradiation. The horizontal line in each graph denotes the state of the original untreated and non-irradiated sample.



**Figure 3.1a.** The decreases in L\* for TMP (left) and BTMP (right) handsheets treated with mercaptans and irradiated for 3 hours by Ultravitalux sunlamps.



**Figure 3.1b.** The increases in b\* for TMP (left) and BTMP (right) handsheets treated with mercaptans and irradiated for 3 hours by Ultravitalux sunlamps.



**Figure 3.1c.** The increases in  $a^*$  for TMP (left) and BTMP (right) handsheets treated with mercaptans and irradiated for 3 hours by Ultravitalux sunlamps.

Both the TMP and BTMP untreated controls experienced reversion manifesting as darkening (decrease in  $L^*$ , Figure 3.1a), yellowing (increase in  $b^*$ , Figure 3.1b) and a slight increase in redness (increase in  $a^*$ , Figure 3.1c), with each change being larger for BTMP than TMP. This concurs with previous findings discussed in Chapter 2. The acetone treated controls did not differ significantly from the untreated controls, confirming the solvent to have had an insignificant effect on the reversion of the handsheets.

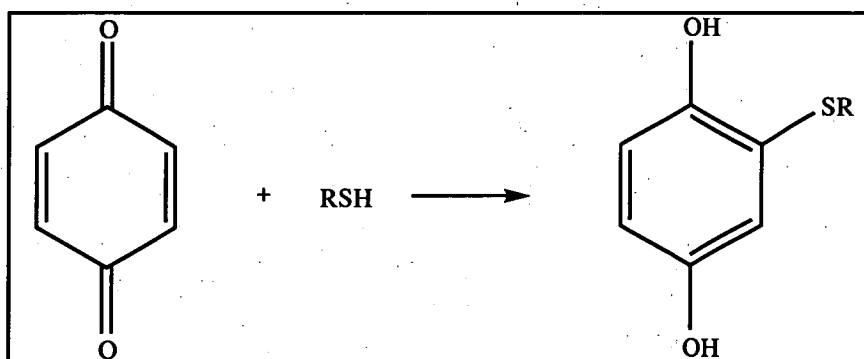
Prior to irradiation, each mercaptan imparted an initial bleaching effect on both sets of handsheets, with an increase in whiteness ( $L^*$ ) and decrease in yellowness ( $b^*$ ). Results for TMP revealed an almost complete removal of redness, with  $a^*$  being reduced to almost zero. BTMP had already undergone a complete removal of red colouration by the hydrogen peroxide bleaching, (i.e.  $a^*$  had become negative). Each mercaptan extended this bleaching effect further, with an apparent rise in greenness occurring (i.e.  $a^*$  became more negative). The magnitudes of the initial bleaching by each mercaptan were similar, and in each case appeared to be larger for TMP than for BTMP. This could be due to a fewer number of bleachable coloured species initially present in the peroxide bleached handsheets.

Washing with acetone decreased the whiteness ( $L^*$ ) of the treated handsheets to a small degree for both TMP and BTMP, but did not significantly affect the removal of yellowness ( $b^*$ ) or redness ( $a^*$ ) the mercaptan treatments had afforded. Therefore washing did not significantly affect the initial bleaching of the three mercaptans.

Each mercaptan inhibited the reversion observed for both sets of untreated controls, but not to the same degrees of efficiency. EGB was the best inhibitor with darkening (decrease in  $L^*$ ) and reddening (increase in  $a^*$ ) effectively halted, and yellowing (increase in  $b^*$ ) greatly reduced for both TMP and BTMP. For treatments with both Thg and Thl, darkening (decrease in  $L^*$ ) and yellowing (increase in  $b^*$ ) were greatly reduced for both TMP and BTMP, and reddening (increase in  $a^*$ ) was effectively halted for BTMP. For TMP reddening occurred to the same extent as for the untreated control, but this was very small and not greatly significant. The inhibition of reversion observed by the Thg treatment was slightly better than that observed for the Thl treatment.

Washing out the mercaptans with acetone after treatment, but before irradiation, completely destroyed the inhibition ability of each mercaptan acting on both TMP and BTMP. For TMP this washing even resulted in an increase in reversion with respect to the untreated control, as measured by each colour parameter. For BTMP an increased yellowing ( $b^*$ ) occurred with respect to the untreated control on irradiation, but darkening ( $L^*$ ) and reddening ( $a^*$ ) proceeded to the same extent as the untreated control. These results indicate that the inhibition observed for treatments with each mercaptan was independent of the initial bleaching reactions seen with each treatment. Also, for effective inhibition of light-induced reversion of TMP and BTMP, the mercaptans must remain within the paper matrix during irradiation. Thus it is unlikely that inhibition occurs from an initial reaction which prevents light-induced darkening reactions from occurring. It is more likely that an ongoing series of inhibitory processes take place during irradiation. Possible inhibitory processes which require the presence of the inhibitor during irradiation include:

a. Removal of coloured species as they are formed. For example the mercaptans could remove coloured quinone species as they form, by undergoing Michael-type addition reactions of the  $-SH$  groups to the quinone species. This process, proposed by Cole et al.<sup>97</sup> (see Section 1.3.5), is reproduced in Figure 3.2.



**Figure 3.2.** Michael-type addition of thiols to quinones<sup>97</sup>.



b. Shielding or protecting the photo-reactive species in lignin from UV radiation. For example, the mercaptans could behave as UV absorbers, which absorb UV radiation and redistribute it as non-harmful thermal energy (see Section 1.3.2).

c. Removal of radical species and/or intermediates produced during irradiation via hydrogen donation or radical scavenging by the mercaptans. This would prevent further propagations of the radical species, and prevent the radical intermediates from reacting further into yellow products (see Section 1.3.5).

d. The mercaptans may quench the excited states of lignin functional groups, which had been induced by absorption of UV radiation (see Section 1.3.3).

### 3.1.4 Conclusions

- Both TMP and BTMP handsheets were bleached by the three mercaptans tested, with the extent of bleaching being similar for each mercaptan.
- This bleaching was greater for TMP handsheets than for BTMP handsheets. This is due to the TMP handsheets initially containing a greater number of bleachable coloured components than the already bleached BTMP handsheets.
- Inhibition of reversion also occurred by each mercaptan, but not to the same degrees of efficiency. EGB afforded an excellent, almost complete inhibition while acting on both TMP and BTMP handsheets. Thg and Thl treatments resulted in a moderate degree of inhibition, with Thg being slightly more efficient than Thl.
- Washing the mercaptans from both sets of handsheets after treatment but prior to irradiation did not significantly affect the initial bleaching action observed. It did, however, completely destroy the inhibition ability of each mercaptan. Thus the inhibition of reversion observed by each mercaptan was independent of their initial bleaching reactions.
- The destruction of inhibition ability by the washing procedure suggests that the mercaptan must remain within the paper matrix throughout irradiation for effective inhibition to occur. There are several possible mechanisms of inhibition that would comply with this requirement. For example the mercaptans may act as UV absorbers, excited state quenchers, hydrogen donors, or radical scavengers. They could also remove coloured products of irradiation as they are formed.

## **3.2 Further Analyses**

### **3.2.1 Introduction and experimental details**

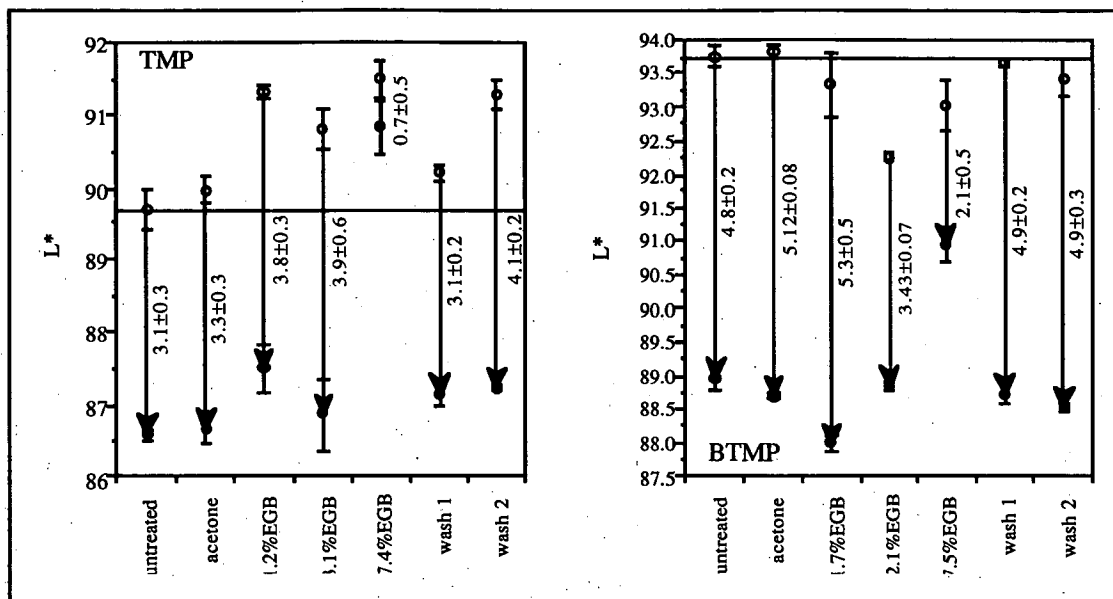
EGB was established as a superior inhibitor for both TMP and BTMP light-induced reversion in the previous section at a load of approximately 14% on paper. This is quite a high load of chemical and certainly impractical for economic (and environmental) reasons. Therefore lower loads of EGB were applied to TMP and BTMP handsheets and tested for their ability to inhibit reversion. Further acetone-washing stages were also carried out, including an immediate washing after treatment (referred to as “wash 1”) and a delayed washing (24 hours) post treatment (referred to as “wash 2”). Each washing procedure was performed after treatment of the handsheets with the highest load of EGB presented in this section.

A new batch of handsheets were required, and were made following the procedures described in Chapter 2. Therefore the results for the irradiated controls (i.e. untreated and solvent samples) have again been presented to accommodate for small fluctuations between batches. As the relative extents of reversion caused by irradiation for these controls did not differ greatly from those discussed in the previous section, they will not be discussed here in detail. The results will still be presented, however, for comparative purposes. The length of irradiation was extended to five hours, to see if the inhibition ability of EGB could persist.

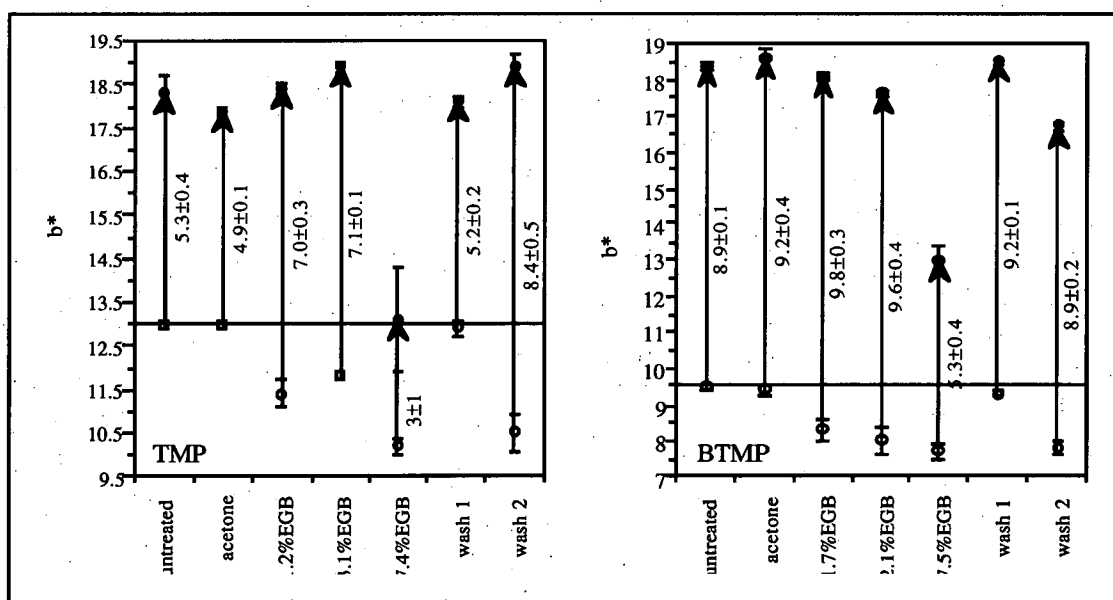
Analyses of the inhibition observed by EGB treatment was also extended to include measures of the extent of chromophore production (by measurements of the absorption coefficient,  $k$ ), and construction of UV-visible absorption difference spectra. All measurements and calculations ( $L^*$ ,  $a^*$  and  $b^*$ , absorption coefficient, and UV-visible absorption difference spectra) were performed following the procedures previously described in Chapter 2. The UV-visible absorption difference spectra were constructed with EGB treated samples measured against a reference consisting of untreated controls, and irradiated samples measured against a reference of non-irradiated controls.

### **3.2.2 Results and discussion**

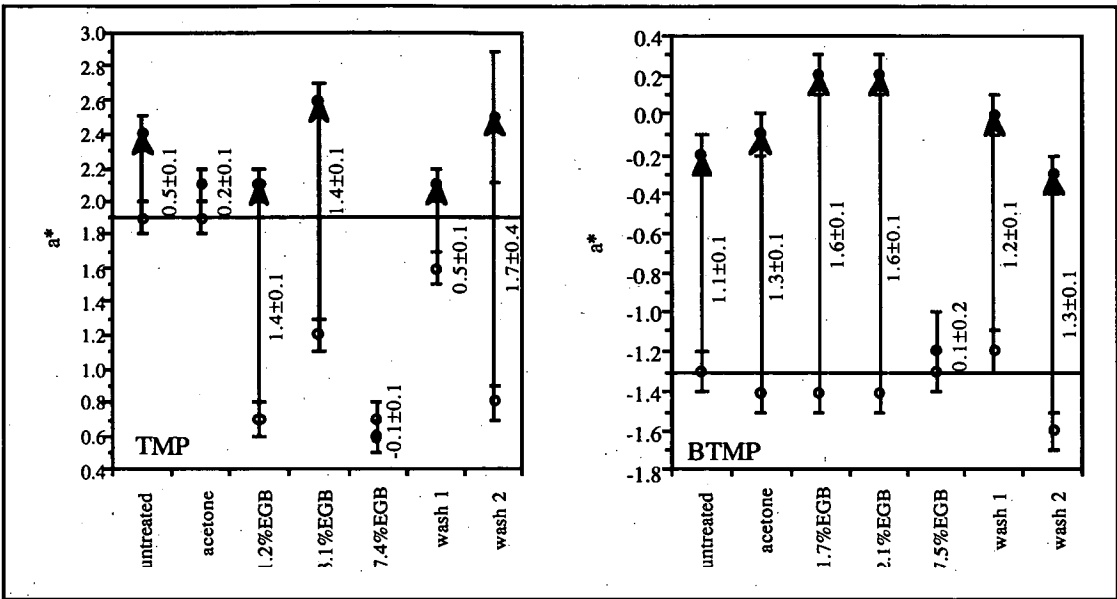
The tristimulus colour parameters  $L^*$ ,  $a^*$  and  $b^*$  for handsheets treated with the various loads of EGB and irradiated are shown in Figures 3.3a, b and c for both TMP (left) and BTMP (right). These figures are similar to those already described in Section 3.1.3 (Figures 3.1a, b and c). The absorption coefficients,  $k$ , are shown in similarly constructed plots in Figure 3.4 for TMP (left) and BTMP (right).



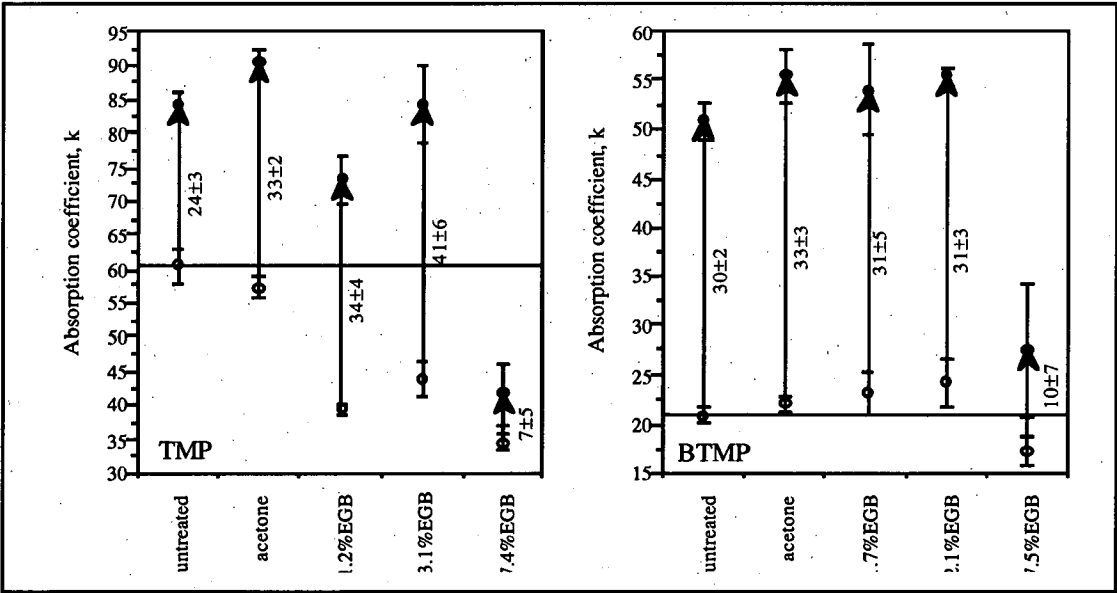
**Figure 3.3a.** The decreases in L\* for TMP (left) and BTMP (right) handsheets treated with various loads of EGB and irradiated for 5 hours by Ultravitalux sunlamps.



**Figure 3.3b.** The increases in b\* for TMP (left) and BTMP (right) handsheets treated with various loads of EGB and irradiated for 5 hours by Ultravitalux sunlamps.



**Figure 3.3c.** The increases in  $a^*$  for TMP (left) and BTMP (right) handsheets treated with various loads of EGB and irradiated for 5 hours by Ultravitalux sunlamps.



**Figure 3.4.** The increases in the absorption coefficients,  $k$  ( $\text{g/m}^2$ )<sup>-1</sup>, for TMP (left) and BTMP (right) handsheets treated with various loads of EGB and irradiated for 5 hours by Ultravitalux sunlamps.

### *Untreated samples*

As found previously in both Chapter 2 and Section 3.2, the irradiation-induced reversion, as measured by the tristimulus colour parameters  $L^*$ ,  $a^*$  and  $b^*$ , was apparently larger for BTMP than TMP. In Chapter 2 concerns as to the reliability of conclusions drawn from these results were presented. It was noted there that the BTMP handsheets may not have actually undergone greater reversion. Instead, being originally whiter and brighter, they may have just been more sensitive to induced colour changes than the originally darker TMP handsheets. Comparing the changes in the absorption coefficients,  $k$ , for the two handsheets provides a better perspective on this, as the absorption coefficient is a value which is directly proportional to the amount of chromophores (absorbing at a given wavelength) in the handsheets. Figure 3.4 confirms that chromophores were produced by irradiation for both TMP and BTMP, as increases in the absorption coefficients,  $k$ , occurred. Like the colour parameters discussed previously, this chromophore production (or increase in  $k$ ) was greater for BTMP than for TMP. The ratios of the changes in each measurement for BTMP over TMP on irradiation are shown below:

Parameter	Ratio of changes induced by irradiation for BTMP / TMP
$L^*$	$1.6 \pm 0.2$ (decreasing)
$b^*$	$1.7 \pm 0.2$ (increasing)
$a^*$	$2.4 \pm 0.7$ (increasing)
$k$	$1.3 \pm 0.3$ (increasing)

The ratios of the decrease in  $L^*$  and increase in  $b^*$  for BTMP over TMP on irradiation are comparable to that of the increase in the chromophore content, or absorption coefficient,  $k$ . Therefore the elevated changes in  $L^*$  and  $b^*$  for BTMP over TMP were not a result of a higher sensitivity to changes in these parameters for BTMP, but were indeed due to a greater extent of reversion.

The ratio of the increase in  $a^*$  for irradiated BTMP over TMP, however, exceeded that for the absorption coefficient,  $k$ . The peroxide bleaching had increased the whiteness ( $L^*$ ) and decreased the yellowness ( $b^*$ ), redness ( $a^*$ ), and the chromophore content ( $k$ ) of TMP. For  $a^*$  this bleaching was complete, with values undergoing a change in sign from positive (red) values to slightly negative (green) values. This indicates that all red chromophores were removed by peroxide bleaching. Therefore it is plausible that peroxide bleached handsheets would exhibit a higher sensitivity to increases in redness, or  $a^*$ , than TMP handsheets, as they originally lack this colouration.

## *Ethylene glycol bistioglycolate treatment*

### *The bleaching effect on TMP handsheets*

Each EGB treatment caused a bleaching in TMP, as was revealed by an initial increase in whitening or  $L^*$  (Figure 3.3a), a removal of yellow colouration (decrease in  $b^*$ , Figure 3.3b), and a removal of red colouration (decrease in  $a^*$ , Figure 3.3c). This bleaching was also confirmed by a reduction in the chromophore content, indicated by a decrease in the absorption coefficient,  $k$  (Figure 3.4). The extent of this bleaching was not greatly affected by the percent loads of EGB presented here, with the highest load being only slightly more efficient than the lowest. This bleaching was not, however, as efficient as the bleaching observed in Section 3.1 for an excessive (14%) load of EGB. So, while bleaching of TMP is more efficient with excessive loads of EGB, it is still significant when the load is reduced.

When TMP handsheets were washed immediately after treatment with EGB (wash 1), the bleaching as measured by the removal of yellowness ( $b^*$ ) was ineffective, and whitening ( $L^*$ ) and redness removal ( $a^*$ ) were partially ineffective. Delayed washing (wash 2), on the other hand, did not significantly affect the bleaching responses. These results suggest that an immediate bleaching response occurred, which involved a partial removal of red chromophores or colour ( $a^*$ ). A delayed bleaching response followed, which involved further removal of red chromophores and a removal of yellow chromophores (decrease in  $b^*$ ). That is, EGB may bleach TMP in two stages, with a preferential removal of red chromophores followed by a slower removal of yellow species.

### *The bleaching effect on BTMP handsheets*

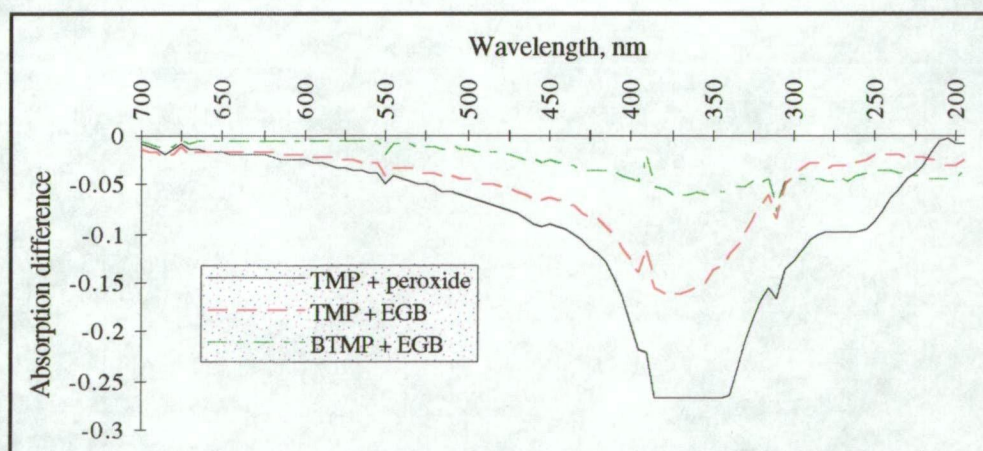
No whitening was observed (in fact a small darkening or decrease in  $L^*$  occurred, see Figure 3.3a) by EGB treatment. Nor was there a decrease in red colouration (or  $a^*$ , Figure 3.3c). This is a sharp contrast with the bleaching effect on BTMP of the 14% EGB load, discussed in the previous section. This, however, is probably not an indication of a requirement for excessive loads of EGB in order to efficiently bleach BTMP handsheets. Instead, it is likely to be a result of the greater efficiency of the peroxide bleaching process in the current batch of handsheets. This is evident as the untreated samples were initially whiter (with a greater  $L^*$  value) and less coloured (lower  $b^*$  and  $a^*$  values) than those from the previous section. Therefore the current batch of BTMP handsheets contained less bleachable components for the EGB treatments to act on.



The bleaching that was observed as a decrease in  $b^*$  (Figure 3.3b), caused by treatment with EGB indicated that bleaching had occurred via a removal of yellow chromophores. As with TMP discussed above, the extent of this bleaching was not greatly dependent on the percent loads of the mercaptan. The absorption coefficient,  $k$  (Figure 3.4) also confirmed a bleaching effect (i.e. a removal of chromophore content, or decrease in  $k$ ). This latter effect was small, however, and was only observed for the higher percent loads of EGB.

Both immediate washing (wash 1) and delayed washing (wash 2) removed the slight darkening which was observed for EGB treatments, possibly by leaching out darkened species. While the immediate washing (wash 1) deactivated the slight bleaching or removal of yellow species (observed by  $b^*$ ), delayed washing (wash 2) did not affect this bleaching. This suggests that the removal of yellow species is a delayed reaction, requiring an extended retention of EGB. A similar effect was also observed for TMP above.

Therefore it appears that both hydrogen peroxide and EGB bleach TMP by removing red (reduction in  $a^*$ ) and yellow (reduction in  $b^*$ ) coloured species. For EGB, the red chromophores are removed preferentially over the yellow chromophores. The UV-visible absorption difference spectra for both of these bleaching processes (against non-bleached counterparts) allow for comparisons of the mode of action by each bleaching process to be made. These spectra are shown in Figure 3.5, (that is, the difference spectra for peroxide bleached TMP against unbleached TMP, (TMP+peroxide); EGB bleached TMP against unbleached TMP, (TMP+EGB); and TMP bleached with peroxide and EGB against TMP bleached with peroxide only, (BTMP+EGB)).

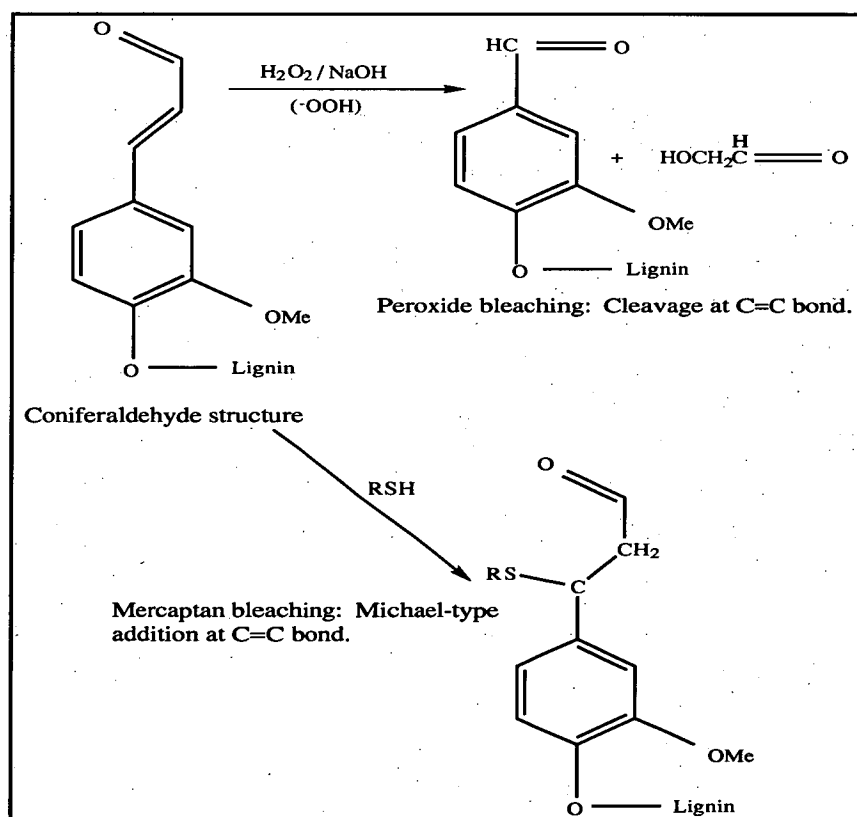


**Figure 3.5.** UV-visible absorption difference spectra for hydrogen peroxide bleached (BTMP) and EGB bleached TMP handsheets minus non-bleached samples.

All spectra in Figure 3.5 are identical, except for their intensities, with a reduction in absorption around 360nm. In Chapter 2 it was suggested that hydrogen peroxide bleaching occurred via removal of coniferaldehyde species<sup>41</sup>, which absorb in this region. Therefore it is possible that EGB also bleaches TMP via a removal of coniferaldehyde species. The intensity of this “removal” peak at 360nm is greater for EGB acting on TMP than EGB acting on BTMP. This is because the peroxide bleaching had removed much of this species already.

Although the intensity of the removal peak for peroxide acting on TMP appears much greater than either of the EGB treatments, it cannot be concluded that peroxide is a more efficient bleaching agent than EGB, as different bleaching conditions were used. For example, peroxide was applied to a pulp slurry while EGB was applied to handsheets, and peroxide had a much longer retention time. We can only safely conclude that with the different bleaching methods used, peroxide resulted in a more efficient removal of coniferaldehyde species.

It is possible that the bleaching, or removal of coniferaldehyde species, by hydrogen peroxide occurs via cleavage of the side chain C=C bond, as previously cited in Chapter 2. The bleaching of these species by mercaptans, on the other hand, may occur via a Michael-type addition of the thiol at the C=C bond, as suggested by Cole et al.<sup>97</sup> and cited in Section 1.3.5. These possibilities are summarised in Figure 3.6.



**Figure 3.6.** Possible mechanisms for the bleaching action of hydrogen peroxide and mercaptans acting on coniferaldehyde groups in lignin.



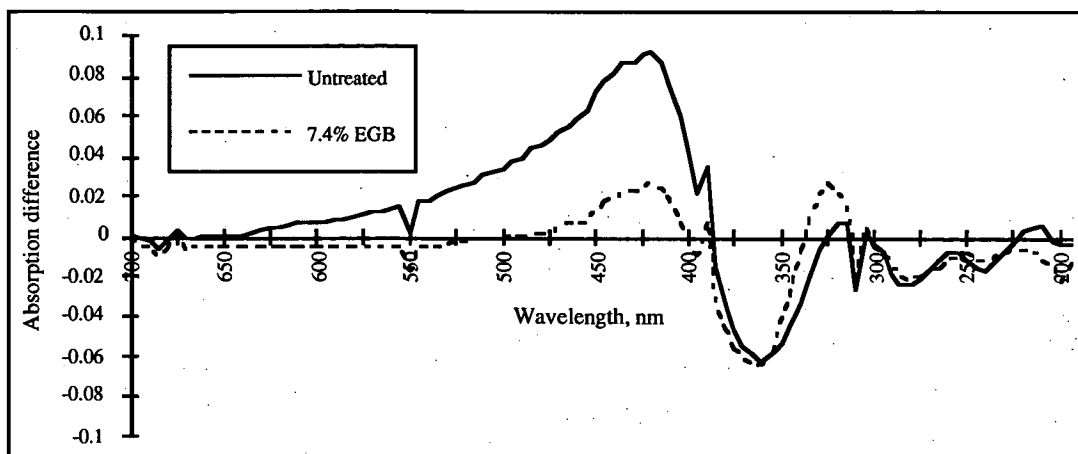
### *Inhibition of the light-induced reversion of TMP handsheets*

The highest load of EGB either completely inhibited or almost completely inhibited the darkening (decrease in  $L^*$ , Figure 3.3a), red shift (increase in  $a^*$ , Figure 3.3c) and yellowing (increase in  $b^*$ , Figure 3.3b), compared to the untreated sample. Reversion, as shown by an increase in the chromophore content (or absorption coefficient,  $k$ ), was also revealed to be largely inhibited with the highest load of EGB against the untreated sample (Figure 3.4). The lower concentrations, however, not only failed to inhibit the reversion, but also appeared to increase it, with greater darkening (decrease in  $L^*$ ), reddening (increase in  $a^*$ ), yellowing (increase in  $b^*$ ), and increases in chromophore contents ( $k$ ), compared to the untreated control.

Immediate washing after the application of EGB to the handsheets (wash 1) destroyed the inhibition ability of EGB, with changes in each colour parameter occurring to the same extent as the untreated controls on irradiation. Delayed washing (wash 2) not only destroyed the inhibition ability of EGB, but also resulted in an enhanced discolouration over the untreated control for each colour parameter. These results confirm the requirement for mercaptans to remain in the handsheet for effective inhibition of light-induced reversion.

One possible explanation for the enhanced reversion seen in the delayed washing samples (compared to the immediate wash) could be that the slower bleaching reaction (i.e. the removal of yellow chromophores, see above) could be dependent on the presence of excess EGB. For example, it could be a reaction in equilibrium, with the presence of excess EGB maintaining the reaction towards production of non-coloured species. Removal of the excess EGB by washing could slowly push this equilibrium in the opposite direction, and therefore see a replenishment of the removed coloured species. Therefore two separate sources of coloured species in such irradiated samples could occur, those due to reversal of the bleaching process and those due to photo-induced reversion, creating an appearance of enhanced discolouration.

The UV-visible absorption difference spectra for irradiated TMP and irradiated TMP treated with EGB against their non-irradiated counterparts are shown in Figure 3.7. It should be noted that spectra of the acetone control and lower loads of EGB were also taken, but did not differ from the untreated control in either shape or intensity (which confirms their lack of inhibition). Therefore they are not presented here.



**Figure 3.7.** UV-visible absorption difference spectra for irradiated TMP handsheets and irradiated TMP handsheets treated with EGB, against their non-irradiated counterparts.

The UV-visible difference spectra for irradiated TMP against non-irradiated TMP has already been discussed in Chapter 2 (see Figure 2.5b), with suggestions that the large dip around 360nm corresponds to a photo-induced removal of coniferaldehyde structures which absorb in this region. The reaction scheme for this process was shown in Reaction 2, Chapter 2, with products including conjugated carbonyls which absorb around 300-330nm. This was consistent with the appearance of a peak in this region of the spectra. The large peak at around 430nm, the “yellowing” peak, was attributed to the formation of *o*-quinones. The spectra for irradiated TMP in Figure 3.7 is consistent with all these findings. As the only significant difference between this spectra and that for the EGB treated sample is a large decrease in the 430nm peak, it can be concluded that EGB has inhibited reversion by inhibiting the formation of *o*-quinone species. As this peak still exists however, their formation has not been completely stopped, and it also appears that EGB has not altered the reversion pathways. This suggests a mechanism of inhibition in which EGB removes or inhibits the formation of coloured species without interrupting the reversion chemistry. For example, removing coloured species as they are formed, or preferentially absorbing UV light, and thereby shielding photo-reactive groups in lignin.

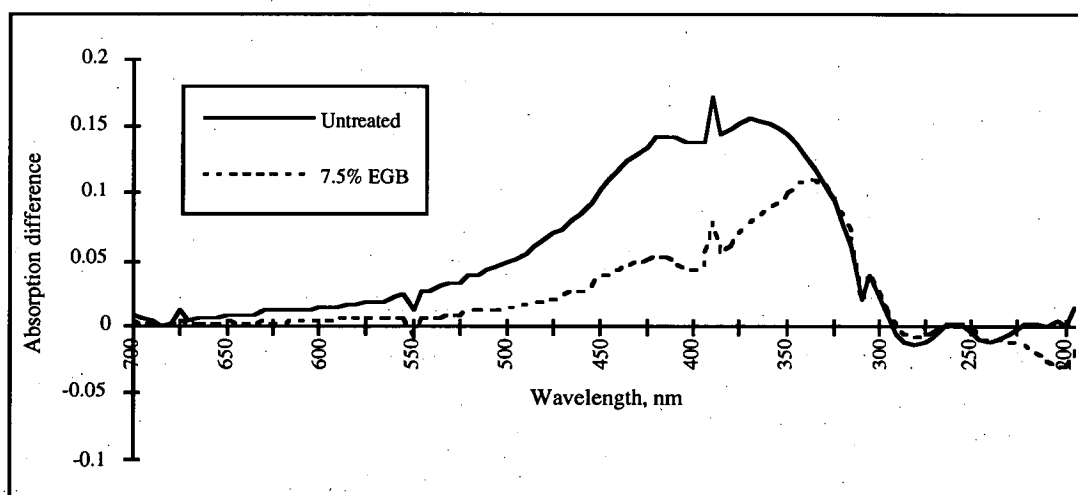
#### *Inhibition of the light-induced reversion of BTMP handsheets*

The lowest EGB load (1.7%) on BTMP handsheets exerted no inhibition of reversion in any of the colour parameters or the absorption coefficient (see Figures 3.3 and 3.4). In fact, reversion appeared to have been increased slightly by this treatment. The 2.1% load afforded a small inhibitory effect on the light-induced darkening ( $L^*$ ) only. The highest load (7.5%), however, inhibited reversion to a large extent. Photo-induced darkening (decrease in  $L^*$ ), yellowing (increase in  $b^*$ ) and chromophore

production (increase in  $k$ ) were all significantly inhibited by this treatment, while reddening (increase in  $a^*$ ) was completely inhibited.

Both washing procedures completely destroyed the inhibition ability of EGB with respect to changes in all colour parameters. Unlike TMP discussed above, however, there was no significant enhancement of reversion after wash 2 (the delayed washing process). This supports the suggestion made previously, that the enhanced reversion of EGB treated TMP after delayed washing was a combined effect of the formation of coloured species due to reversion and the reformation of coloured species previously removed by bleaching reactions. For BTMP, reversion of these washed samples involved the formation of coloured species, but as there was little initial bleaching by EGB, the reformation of previously EGB bleached species was minimal.

The UV-visible absorption difference spectra for irradiated BTMP and irradiated BTMP treated with EGB against their non-irradiated counterparts are shown in Figure 3.8.



**Figure 3.8.** UV-visible absorption difference spectra for irradiated BTMP handsheets and irradiated BTMP handsheets treated with EGB, against their non-irradiated counterparts.

The UV-visible absorption difference spectrum for irradiated BTMP has already been discussed in Chapter 2 (see Figure 2.5a), with the large peak observed around 430nm, (commonly referred to as the “yellowing peak”), having been attributed to the formation of *o*-quinone species. Chapter 2 revealed an identical spectrum to that shown in Figure 3.8, and it was unclear whether the large increase in absorption around 400nm was due to one broad peak, or one peak with a shoulder at 360nm, as the source change divot had clouded results. In Figure 3.8, the spectra for the irradiated BTMP and EGB treated samples appeared similar except for their

intensities. The absorption peaks for the EGB treated sample, however, were better distinguished, and revealed two defined peaks at 430nm and 325nm, and one shouldering peak at 360nm. Thus it is probable that the broader spectrum observed for irradiated BTMP also contained two peaks and a shouldering peak like those for the EGB treated sample. Therefore it can be assumed that during irradiation both the peroxide bleached sample and the EGB treated sample had undergone a similar formation of quinones (absorbing at 430nm), and two other species (absorbing at 360nm and 325nm).

For the EGB treated BTMP sample, each absorption peak formed after irradiation was less intense than those formed for the untreated control (see Figure 3.8). Therefore, the production of coloured products (quinones, coniferaldehyde species, and conjugated ketones) was reduced, but not entirely prevented, by the EGB treatment. Like TMP discussed above, the shapes of the absorption difference spectra for the EGB treated sample and untreated control were similar after irradiation. Therefore it appears that the inhibition of reversion of BTMP by EGB also proceeds via mechanisms which do not alter the reversion pathways.

#### *Further observations*

Both bleaching processes were previously found to remove coniferaldehyde structures from TMP, which absorb around 360nm. The shouldering peaks at 360nm in Figure 3.8, for both the BTMP sample and the EGB treated BTMP sample, could be due to a reformation of these coniferaldehyde species during irradiation. For TMP bleached with EGB and irradiated, however, no reformation of coniferaldehyde species was apparent, as there was no absorption peak observed at 360nm in the spectrum shown in Figure 3.7. One explanation for this could be that the peroxide bleaching was rendered reversible during irradiation, while the EGB bleaching was not, (at least for the samples presented here, which were treated with higher loads of EGB and not washed after treatment). For the peroxide bleaching to be rendered reversible, the initial reaction products would need to recombine (i.e. the vanillin-like structure and hydroxy ketone, see Figure 3.6). As the handsheets were washed thoroughly after the peroxide bleaching process (see Section 2.2.1), however, this would be highly improbable. It is more likely that alternative photo-induced reactions had occurred for the peroxide bleached handsheets that involved reactants that were not present in the EGB bleached handsheets, resulting in a reformation of coniferaldehyde structures. This would indicate that while both peroxide and EGB remove coniferaldehyde structures, their bleaching mechanisms are likely to be different, as previously suggested in Figure 3.6.

The shoulder at 360nm for the irradiated EGB treated BTMP sample in Figure 3.8 was relatively less intense with respect to that of the irradiated BTMP sample. For irradiated BTMP, the absorption at 360nm would be a result of residual coniferaldehyde species plus those that were reformed by irradiation. For the EGB bleached sample, however, the residual coniferaldehydes would have been removed by EGB. Therefore, the absorption at 360nm would be less intense as it would result only from the coniferaldehyde species which were reformed by irradiation. This would suggest that the reactants in the peroxide bleached handsheets which are responsible for the reformation of coniferaldehyde were unaffected by EGB treatment.

The reintroduction of previously removed coniferaldehyde species would also explain the greater extent of reversion found for BTMP over TMP. While both quinone species and coniferaldehyde species were formed during the reversion of BTMP, only the quinone species were formed for TMP. In fact for TMP, coniferaldehyde species were found to be removed during irradiation (see above, Figure 3.7). A mechanism has been proposed for this removal of coniferaldehyde species in TMP during irradiation, and was cited in Chapter 2 (Reaction 2). In this mechanism, two products were revealed, one of which was a conjugated ketone species, which absorbs at 330nm. The spectra for irradiated TMP did indeed reveal an increase in absorption at 330nm, for both the TMP sample and the EGB treated sample. This is also the same spectral region as the final absorption peak observed for the irradiated BTMP and BTMP treated with EGB samples in Figure 3.8. Therefore, it appears that during irradiation of these bleached samples, the reformed coniferaldehyde species may also have been subsequently removed by irradiation, resulting in the formation of conjugated ketones. If this were the case, then the reformation of these species was the dominating reaction.

### 3.2.3 Conclusions

#### *Reversion of TMP and BTMP*

- The photo-induced reversion of both TMP and BTMP resulted in the formation of coloured quinone species. BTMP underwent a greater extent of reversion than TMP. This was due to the reformation of coniferaldehyde species in BTMP during irradiation, where these species had been previously removed by the bleaching process. By contrast, coniferaldehyde species were actually removed during irradiation for TMP. A third product of irradiation was found for both TMP and BTMP. These were a conjugated ketone species and are a byproduct from the

UV-induced removal of coniferaldehyde species in TMP. These species are accounted for in BTMP, as the reformed coniferaldehydes are also removed during irradiation. Their removal during irradiation, however, is slower than their reformation.

### ***Bleaching of TMP and BTMP by EGB***

- Bleaching of both TMP and BTMP handsheets by EGB was not greatly dependent on the load of the mercaptan, with high loads (about 7.5%) being only slightly more efficient than low loads ( $\leq$  about 3%). While this bleaching was good, it was generally not as efficient, however, as the bleaching observed using excessive loads of EGB (14-16%).
- Bleaching of TMP by EGB is similar to alkaline peroxide bleaching in that it involves the removal of coniferaldehyde species. The mechanisms of these two bleaching agents, however, are likely to be different. While peroxide bleached handsheets undergo a reformation of coniferaldehyde species during irradiation, EGB bleached handsheets do not (at least for relatively high loads of EGB that are not washed out prior to irradiation). This suggests that peroxide bleached handsheets contain photo-reactive species that are distinct from EGB bleached handsheets.
- Bleaching by EGB appears to occur in two stages, involving an initial removal of red chromophores followed by a slower removal of yellow chromophores.
- At least for the slower bleaching action of EGB, (i.e. the removal of yellow species), an equilibrium process may be involved, which requires an excess of EGB to maintain the equilibrium towards bleached, non-coloured, species. Removal of this excess EGB may reverse the equilibrium to favour the reformation of previously bleached coloured species.

### ***Inhibition of the photo-induced reversion of TMP and BTMP by EGB***

- After a delayed washing (i.e. 24 hours after treatment and drying) of EGB treated TMP handsheets, two processes which result in discolouration may occur during irradiation. One involves the light-induced production of coloured species, and the other involves the reformation of species previously removed by bleaching. These combined processes result in the appearance of an enhanced reversion or

discolouration. For similarly treated BTMP handsheets, such enhanced discolouration was not observed. This is because the initial bleaching by EGB was low, and so the reformation of EGB-bleached coloured species was minimal.

- The inhibition of reversion by EGB treatment was much more dependent on the load of EGB on the handsheets than the bleaching reactions were. Low loads of EGB not only failed to inhibit reversion, but in some cases actually enhanced it. High loads of EGB (7.4-7.5%), however, resulted in excellent inhibition of reversion for both TMP and BTMP. At least for TMP, this inhibition was only marginally less efficient than the inhibition afforded by an excess load of EGB (about 14%), despite a longer exposure time.
- EGB did not appear to alter the reversion reactions of both TMP and BTMP, but did result in a decreased formation of coloured products in both cases. EGB could thus inhibit reversion by removing coloured species as they form, or act as a shield or UV absorber, filtering out much UV-light, and therefore lessening the formation of yellow products.

## CHAPTER 4

# PHOTO-INDUCED REVERSION OF MODEL LIGNIN COMPOUNDS

### 4.1 Introduction

As mentioned in Section 1.2 many model lignin compounds (MLCs) have been used in paper chemistry in an attempt to understand what is occurring within the lignin matrix during certain processes. The previous chapter revealed that definite yellowing photo-reactions had occurred in both TMP and peroxide bleached TMP handsheets when they were exposed to irradiation from Ultravitalux sunlamps. A promising inhibition of this yellowing was found when the handsheets were pre-treated with mercaptans, particularly EGB. Analyses of the results however, revealed few clues as to what had actually occurred, due to the complex nature of the lignin-rich pulps. The remainder of this thesis therefore contains research that has been extended using various model lignin compounds. This chapter is a prelude to inhibition studies in that it involves an investigation into what types of MLCs are susceptible to photo-induced reversion and what common factors are involved in the discolouration processes. The results of this chapter can therefore be used to determine which MLCs can be targeted for inhibition studies, which will be discussed in Chapters 5 and 6. Several modifications to the irradiating apparatus were required for MLC studies and these are discussed in Section 4.2.

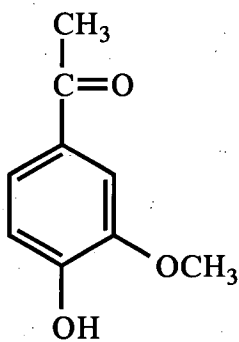
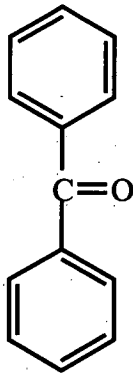
The MLCs chosen for the study were based on several factors, relying heavily on the information discussed in Section 1.2. The MLCs included in the study contain at least one of the following properties:


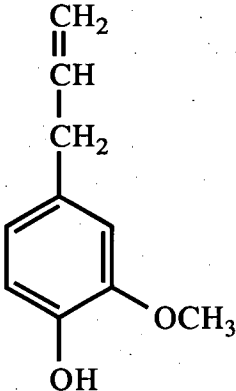
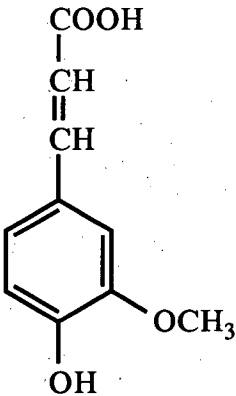
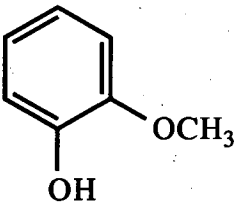
1. It either resembles, or has been shown to be, a structural unit of lignin.
2. It contains functional groups relevant to lignin photo-chemistry. From Section 1.2 it was apparent that three steps in the photo-yellowing processes were fundamental. These were: (a) the initiation, or UV absorption and sensitisation of chromophoric groups; (b) propagation of reaction, or radical formation usually via H-abstraction; and (c) termination by production of yellow products, usually via oxidation. The functional groups relevant to such reactions include possible photo-sensitiser groups (a), possible photo-reaction centres susceptible to H-abstraction (b) and other functional groups possibly involved in the final oxidation of intermediate species to coloured products (c).

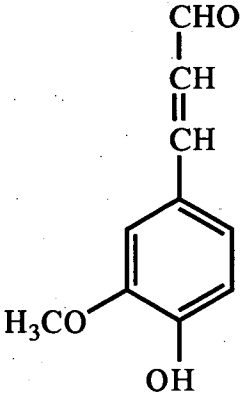
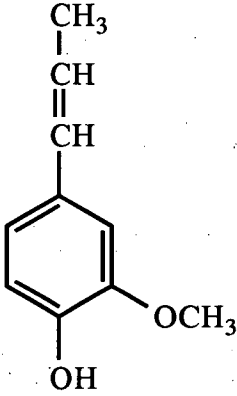
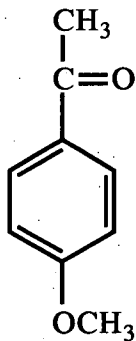


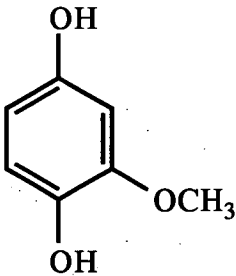
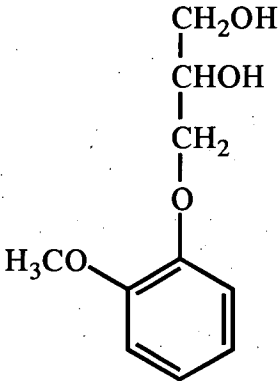
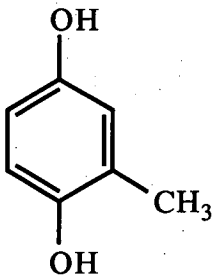
3. The MLC has been implicated as being either a precursor in, or a product of, the photo-yellowing and/or oxidation of lignin.
4. The MLC is thought to be introduced into lignin either through bleaching or mechanical pulping processes.
5. Quinone species.

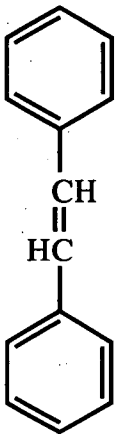
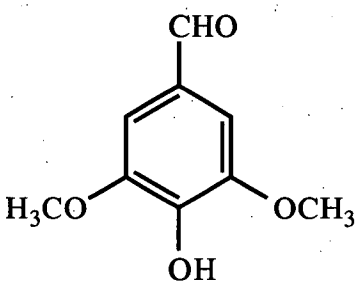
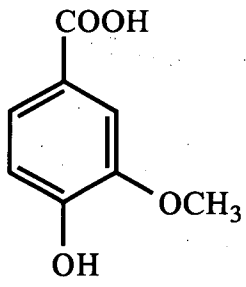
The following pages show the model compounds studied, their structures and brief comments that indicate which of the above properties (1-5) justify their inclusion in the investigation. The postscripts a, b and c indicate functional groups potentially involved in the different photo-reversion steps highlighted in point 2 above (i.e. a = possible photo-sensitiser groups; b = possible photo-reactive centres susceptible to hydrogen abstraction; c = functional groups possibly involved in the final oxidation of species into coloured products).

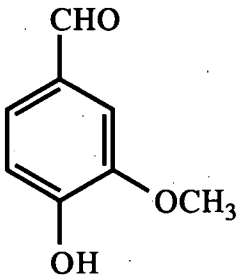
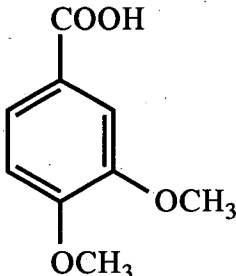
<p>1. Acetovanillone</p> 	<p>98% M.W. 166.18.</p> <p>Fine mustard - yellow powder.</p> <ol style="list-style-type: none"> <li>1. Basic guaiacyl unit in lignin.</li> <li>2. <math>\alpha</math>-carbonyl group<sup>a</sup>, phenolic hydroxyl group<sup>b</sup> and methoxyl group<sup>c</sup>.</li> </ol>
<p>2. Benzophenone</p> 	<p>99% M.W. 182.22.</p> <p>White platelets.</p> <ol style="list-style-type: none"> <li>2. Two phenyl groups<sup>a</sup> and one carbonyl group<sup>a</sup>.</li> </ol>

<p>3. 1,4-Benzoquinone</p> 	<p>98% M.W. 108.10.</p> <p>Fine dark brown powder.</p> <p>5. Basic quinone with no substituents.</p>
<p>4. Eugenol</p> 	<p>99% M.W. 164.20.</p> <p>Colourless liquid.</p> <ol style="list-style-type: none"> <li>1. Basic phenylpropane unit in lignin.</li> <li>2. C=C double bond<sup>a</sup>, phenolic hydroxyl group<sup>b</sup> and methoxyl group<sup>c</sup>.</li> </ol>
<p>5. Ferulic acid</p> 	<p>99% M.W. 178.19.</p> <p>Fine but clumpy pale mustard-yellow powder.</p> <ol style="list-style-type: none"> <li>1. Basic phenylpropane unit in lignin.</li> <li>2. C=C double bond<sup>a</sup>, carboxylic acid end group<sup>a,b</sup>, phenolic hydroxyl group<sup>b</sup> and methoxyl group<sup>c</sup>.</li> <li>3. Could be a product or precursor to photo-yellowing, but uncertainty exists<sup>69,77b</sup>.</li> </ol>
<p>6. Guaiacol</p> 	<p>98% M.W. 124.14.</p> <p>Colourless liquid.</p> <ol style="list-style-type: none"> <li>1. Basic unit of the lignin backbone.</li> <li>2. Phenolic hydroxyl group<sup>b</sup> and methoxyl group<sup>c</sup>.</li> <li>3. Possibly a by-product of irradiation<sup>41</sup>.</li> </ol>

<p>7. 4-Hydroxy-3-methoxy cinnamaldehyde</p> 	<p>98% M.W. 178.19.</p> <p>Mustard coloured powder.</p> <ol style="list-style-type: none"> <li>1. Basic phenylpropane unit in lignin.</li> <li>2. C=C double bond<sup>a</sup>, aldehyde end group<sup>a,b</sup>, phenolic hydroxyl group<sup>b</sup> and methoxyl group<sup>c</sup>.</li> <li>3. Species is removed during irradiation of TMP<sup>41</sup>.</li> <li>4. Species is removed by peroxide bleaching of TMP<sup>68</sup>.</li> </ol>
<p>8. Isoeugenol</p> 	<p>98% M.W. 164.20.</p> <p>Viscous yellow liquid.</p> <ol style="list-style-type: none"> <li>1. Basic phenylpropane unit in lignin.</li> <li>2. C=C double bond<sup>a</sup> phenolic hydroxyl group<sup>b</sup> and methoxyl group<sup>c</sup>.</li> </ol>
<p>9. 4-Methoxyacetophenone</p> 	<p>99% M.W. 150.18.</p> <ol style="list-style-type: none"> <li>2. α-carbonyl group<sup>a</sup> and methoxyl group<sup>c</sup>.</li> </ol>

<p>10. Methoxyhydroquinone</p> 	<p>98% M.W. 140.14.</p> <p>Fine brown powder.</p> <ol style="list-style-type: none"> <li>1. Possibly present in lignin-rich pulps.</li> <li>2. Two phenolic hydroxyl groups<sup>b</sup> and a methoxyl group<sup>c</sup>.</li> <li>3. Plays a major role in the photo-yellowing of lignin-rich pulps<sup>73,74,112</sup>.</li> <li>4. Product or intermediate in peroxide bleaching<sup>73,112,113</sup>.</li> <li>5. Quinonoid structure with a methoxyl substituent.</li> </ol>
<p>11. 3-(4-Methoxyphenoxy)-1,2-propanediol</p> 	<p>98+% M.W. 198.22.</p> <p>Fine but clumpy white powder.</p> <ol style="list-style-type: none"> <li>2. Ether linkage*, non-phenolic hydroxyl groups<sup>a</sup> and methoxyl group<sup>c</sup>.</li> </ol> <p>*(Possibly involved in photo-oxidative cleavage reactions in lignin, see Section 1.2).</p>
<p>12. Methylhydroquinone</p> 	<p>99% M.W. 124.14.</p> <p>Fine pale grey powder.</p> <ol style="list-style-type: none"> <li>2. Two phenolic hydroxyl groups<sup>a</sup>.</li> <li>5. Quinonoid structure with a methyl substituent.</li> </ol>

<p>13. <i>trans</i> Stilbene</p> 	<p>96% M.W. 180.25.</p> <p>Fine white crystals.</p> <ol style="list-style-type: none"> <li>1. Present in lignin (trace amounts).</li> <li>2. C=C bond<sup>a</sup>.</li> <li>3. Possible photo-yellowing product, or precursor to yellow products<sup>70,78,114</sup>.</li> <li>4. Formed on grinding, disc refining and peroxide bleaching of TMP<sup>114</sup>.</li> </ol>
<p>14. Syringaldehyde</p> 	<p>98% M.W. 182.18.</p> <p>Fine very pale yellowish grey powder.</p> <ol style="list-style-type: none"> <li>1. Possible lignin component.</li> <li>2. Aldehyde group<sup>a,b</sup>, phenolic hydroxyl group<sup>b</sup> and two methoxyl groups<sup>c</sup>.</li> <li>3. Product of oxidation and/or irradiation of wood<sup>7</sup>.</li> </ol>
<p>15. Vanillic acid</p> 	<p>97% M.W. 168.15.</p> <p>Fine white powder.</p> <ol style="list-style-type: none"> <li>1. Basic guaiacyl unit in lignin.</li> <li>2. Carboxylic acid substitution<sup>a,b</sup>, phenolic hydroxyl group<sup>b</sup> and methoxyl group<sup>c</sup>.</li> <li>3. Product of oxidation and/or irradiation<sup>4,12,77,78</sup>.</li> </ol>

<p>16. Vanillin</p> 	<p>99% M.W. 152.15.</p> <p>White crystalline powder.</p> <ol style="list-style-type: none"> <li>1. Minor constituent of lignin<sup>69,77a</sup>.</li> <li>2. Phenolic hydroxyl group<sup>b</sup> and methoxyl groups<sup>c</sup>.</li> <li>3. Product or precursor of photo-yellowing and/or oxidation of lignin<sup>7,12,18,70,77,78</sup>.</li> <li>4. Product of peroxide bleaching<sup>77a</sup>.</li> </ol>
<p>17. Veratric acid</p> 	<p>99+% M.W. 182.18.</p> <p>Fine white powder.</p> <ol style="list-style-type: none"> <li>2. Carboxylic acid group<sup>a,b</sup> and methoxyl groups<sup>c</sup>.</li> </ol>

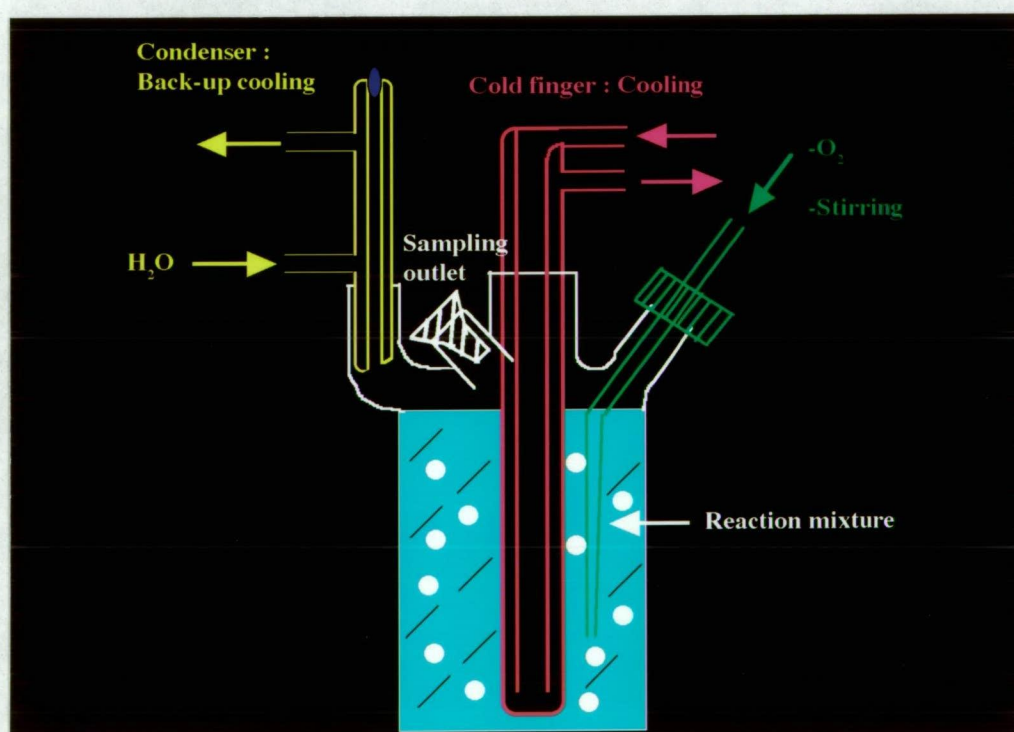
## 4.2 Specific Methods

### 4.2.1 Modifications to the reversion chamber

The reversion chamber introduced in Chapter 2 and used in the subsequent experiments in Chapter 3 was also used to irradiate the model lignin compounds, but several modifications were required beforehand. First, the MLCs were to be irradiated in solution, so suitable vessels were called for. These vessels were required to transmit all radiation wavelengths of relevance to paper photo-chemistry, and needed to be open to air as photo-oxidation reactions were being studied. Due to the heat emitted by the Ultravitalux lamps (see Chapter 2) and the volatility of many organic solvents, a cooling system was required to minimise the evaporative loss of solvent and thermal reversion, and to improve safety.

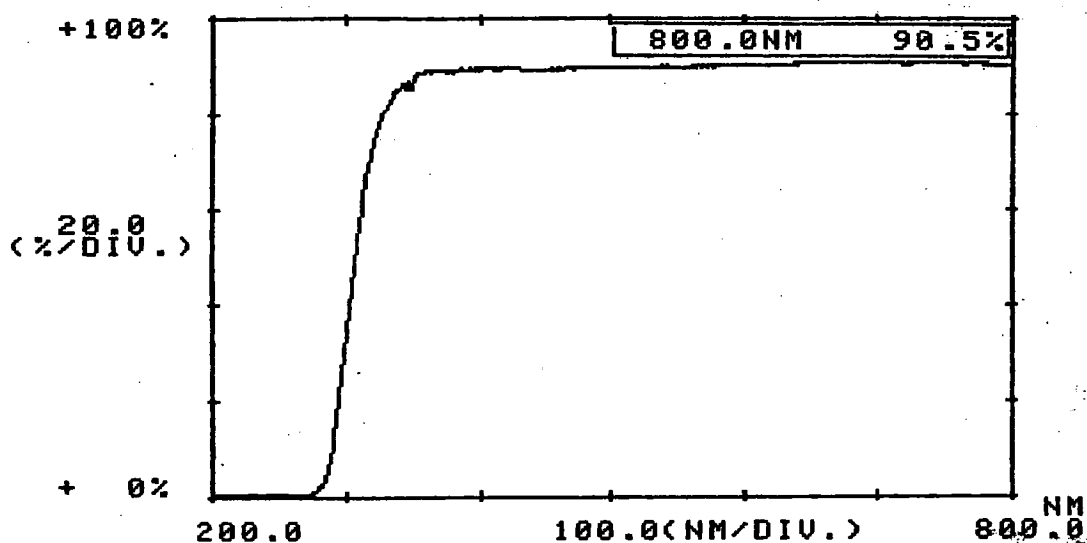
To accommodate these requirements a vessel of 25ml capacity with four outlets/inlets was constructed. A schematic of the vessel is shown in Figure 4.1. Outlet 1 allowed for sampling during irradiation. Inlet 2 allowed oxygen to enter the reaction vessel. The original design included a glass tube entering the solution and attached to an oxygen cylinder. This served the double purpose of providing both

agitation and oxygenation. Long irradiation times, however, meant a rapid consumption of large quantities of oxygen, leading to high cost. The glass tubes were fragile and proved cumbersome, and there were several breakages, while rubber tubes failed to be suitable as they dissolved in the solvent. For these reasons, the oxygen cylinder was removed and tests were performed to gauge its necessity. It was found that the inlet allowed enough atmospheric oxygen to enter the reaction solution naturally, and that the photo-reactions were still able to proceed. To compensate for the loss of the stirring effect and extra oxygenation provided by the original design, the solutions were stirred and aerated well at each sampling point. A cold finger was inserted in the third outlet to keep the solution cool throughout irradiation and the fourth outlet allowed for the attachment of a condenser, which was to prevent solution being lost to evaporation if the cold finger was insufficient or failed mid-experiment.



**Figure 4.1.** Reaction vessel for MLC studies.

The glassware (borosilicate, Duran brand) was tested for its ability to transmit the relevant wavelengths by measuring its ultraviolet-visible transmittance spectrum (see Figure 4.2). The transmittance began to decay at 350nm, cutting off to zero at 300nm. As terrestrial sunlight only contains UV radiation greater than 300nm (see Section 1.1), and the Ultravitalux lamps spectral energy distribution curves (Figure 2.7b, Chapter 2) revealed a significant emission at 350nm, with a decay also down to approximately 300nm, the glassware was deemed suitable for the proposed MLC studies.



**Figure 4.2.** Glassware spectral transmittance.

Finally, the reversion chamber needed to be modified to accommodate the reaction vessels. The sunlamps were moved to the bottom so they could irradiate up into the solutions, and a sample shelf was placed to hold the vessels. Due to the size of the cooling devices the irradiation space became quite small, so two sunlamps were used instead of three to reduce the heat emitted in such a confined space. The area above the sample shelf remained open, while that below was enclosed and painted matt black as with the original design introduced in Chapter 2. The complete reversion chamber is shown in Figure 4.3. Preliminary irradiation performed on water alone revealed that while the chamber walls became too hot to touch, the glass reaction vessels remained cool to the touch, so the cooling devices were deemed adequate.



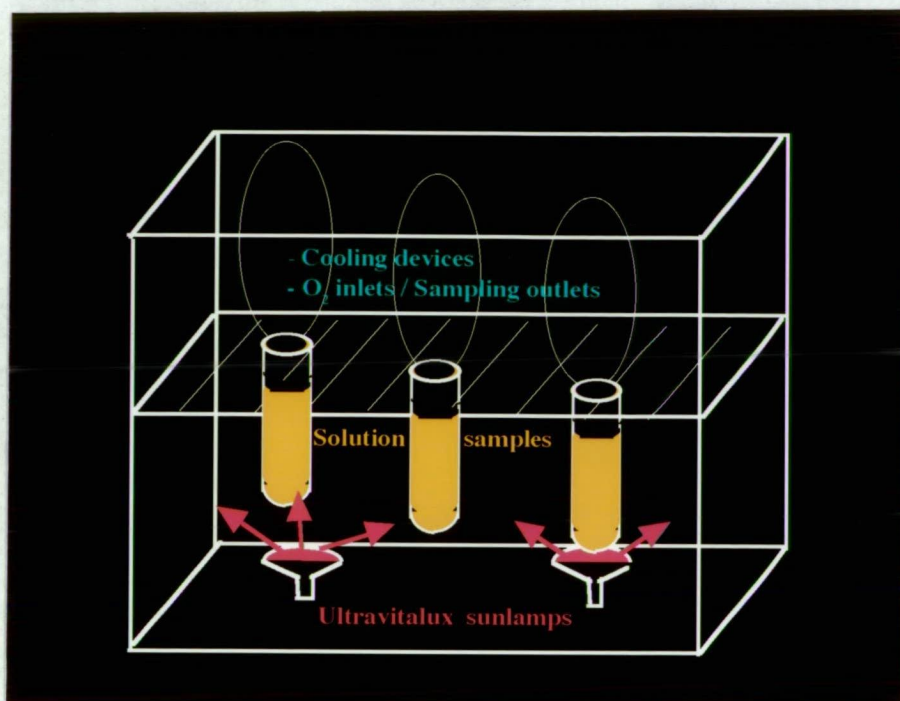


Figure 4.3. Reversion chamber for MLC studies.

#### 4.2.2 Solvent choice

A range of solvents were tested for both evaporative loss in the apparatus, and their ability to dissolve the mercaptan EGB, taking into account requirements for further studies. The results are shown in Table 4.1.

Only diethylene glycol dimethylether (diglyme), dimethylformamide (DMF) and water showed promise for volume retention during irradiation. Of these, water failed to dissolve EGB so it could not be used for further studies. Therefore only the two solvents diglyme and DMF were tested further. Diglyme, being an ether based solvent, has a potential to form explosive peroxides during oxidative irradiation. This did not pose a problem during the trial run, and so it was assumed to be suitable for further experiments (naturally, with appropriate safety measures being readily accessible, see footnote below Table 4.1).

Both solvents were tested for unwanted interactions with the EGB mercaptan and a range of MLCs, which included acetovanillone, 1,4-benzoquinone, guaiacol, 4-hydroxy-3-methoxy cinnamaldehyde, isoeugenol, methoxyhydroquinone and vanillin. The solvents were added to a sample of each MLC and Gas Chromatography-Mass Spectroscopy (GC-MS) was performed to gauge possible interactions. The concentrations of MLCs in the solvents were  $1.8 \pm 0.2$  %. All GC-

MS were performed by the Central Science Laboratory (CSL) in the University of Tasmania. The spectra revealed insignificant solvent-chemical interaction in all cases. Thus DMF was chosen as the preferred solvent, as it is the safer of the two solvents.

**Table 4.1.** Evaporative loss of various solvents and their abilities to dissolve EGB.

Solvent tested.	<sup>a</sup> Volume loss of solvent after irradiation.	Solubility of EGB in solvent.
acetone (b.p. 56.3°C)	100%	soluble
acetonitrile (b.p. 81.6°C)	> 50%	soluble
chloroform (b.p. 61°C)	> 50%	soluble
dichloromethane (b.p. 40°C)	> 50%	soluble
diethylene glycol dimethylether <sup>b</sup> (b.p. 160°C)	negligible after > 1 hour	soluble
diethyl ether <sup>b</sup> (b.p. 35°C)	> 50%	soluble
dimethoxyethane	> 50%	soluble
dimethylformamide (b.p. 153°C)	negligible after > 1 hour	soluble
ethanol (b.p. 78°C)	30% after 30 minutes	not soluble
ethyl acetate (b.p. 77°C)	> 50%	soluble
methanol (b.p. 65°C)	30% after 30 minutes	soluble
tetrahydrofuran (b.p. 66°C)	30% after 30 minutes	soluble
toluene (b.p. 111°C)	20% after 1 hour	soluble
water (b.p. 100°C)	0% after 1 hour	not soluble

<sup>a</sup>Irradiation continued for 30 minutes or less, unless stated otherwise. <sup>b</sup>Note that these ether solvents have the potential to form explosive peroxides in the presence of O<sub>2</sub> during irradiation. Early detection of this is possible by the appearance of a white crystalline residue on the glassware, and neutralisation can be carried out by adding concentrated HCl.

### 4.2.3 Experimental conditions

Each MLC was obtained commercially through Aldrich Chemicals, Pty. Ltd. Air-sensitive chemicals were purged regularly with nitrogen. The MLCs were prepared as 0.5±0.1% solutions in DMF. Irradiations were performed for 12 hours, with samples being extracted every three hours. All samples were stored in glass vials wrapped in aluminium foil, and kept in the dark prior to measurements being taken. The lamps were connected to a timer which switched the power off every 90 minutes, enabling a 10 minute recess to avoid overheating of the lamps. A five minute warming up period was added to each irradiation interval.

#### 4.2.4 Experimental measurements

GC-MS were performed by the Central Science Laboratory (CSL) in The University of Tasmania, and are shown in Appendix A. As in the previous chapters, the absorption coefficients ( $k$ ) and tristimulus colour parameters (CIE  $L^*$ ,  $a^*$ ,  $b^*$ ) were measured to gauge the extent of reversion induced on the MLCs. To measure these parameters a solid medium was required. This was achieved by adsorbing the MLC solution samples onto  $\alpha$ -cellulose filter paper, which is discussed in further detail below.

Diffuse reflectance UV-visible absorption spectra were also examined to monitor reversion induction of the MLCs. Solution UV-visible spectroscopy was the obvious choice but DMF, with a UV absorption cut off at 270nm, produced a large broad peak in this region which swamped out much useful data. Removal of this solvent proved to be a cumbersome task. Several methods were attempted (including GC-MS/TLC/column chromatographic methods to separate species present, extraction of coloured product from the DMF using activated charcoal, and extraction of product using other solvents with absorption maxima ( $\nu_{\max}$ ) occurring at less interfering wavelengths), but due to DMF being quite sticky and having a high boiling point, its removal was messy and difficult. One other removal method considered but untried deserves a mention as a possible course of action for future investigators facing the same problem with this solvent. This is the rotary evaporation of the samples with a secondary solvent to create an azeotropic mixture with the DMF, which should bring the boiling point of DMF down so that its removal would be more manageable. Such a solvent to pair with DMF was not found in standard literature, however.

The following method of dealing with DMF rather than removing it solved the problem of its spectral interference for the purposes of this thesis. This involved converting the samples to a "solid phase" prior to measurements being taken, via adsorption onto alpha-cellulose filter paper (Whatman no. 1, diameter 5.5cm, 65g/m<sup>2</sup>), drying and then taking measurements using the same procedures discussed in Chapter 2. Alpha-cellulose filter paper was chosen as the solid medium as it is pure cellulose, containing no interfering lignin. The UV-visible absorption spectra of the samples in this "solid phase" revealed distinguishable sample / solvent peaks.

Measurements of the colour parameters of these samples using the Elrepho datacolor 2000 were performed as previously described in Chapter 2, with four backing sheets of filter paper. Reliability of the measurements depended heavily on the adsorption technique used, as the results were very sensitive to any changes in technique and large variations were often observed. Thus this "simple task" required great care and

precision to ensure a uniform adsorption of the coloured species. Six different adsorption techniques were tested, and are listed below.

1. The filter paper was placed flat inside a 6cm glass beaker. Enough sample was added to the beaker to cover the filter paper, which was then left to dry. This resulted in an uneven adsorption with visible “watermarks” and blotching in the middle.

2. The filter paper was soaked in 5ml of a 4% solution of MLC in acetone. It was then placed on the underside of an inverted 6cm glass beaker and dried via evaporation. The underside, being slightly convex, prevented pooling in the middle and the consequent blotchiness and watermarks observed in Method 1. This method however also resulted in uneven application of the coloured material.

3. As with Method 2, but DMF was used in place of acetone. This method took too long to evaporate and dry.

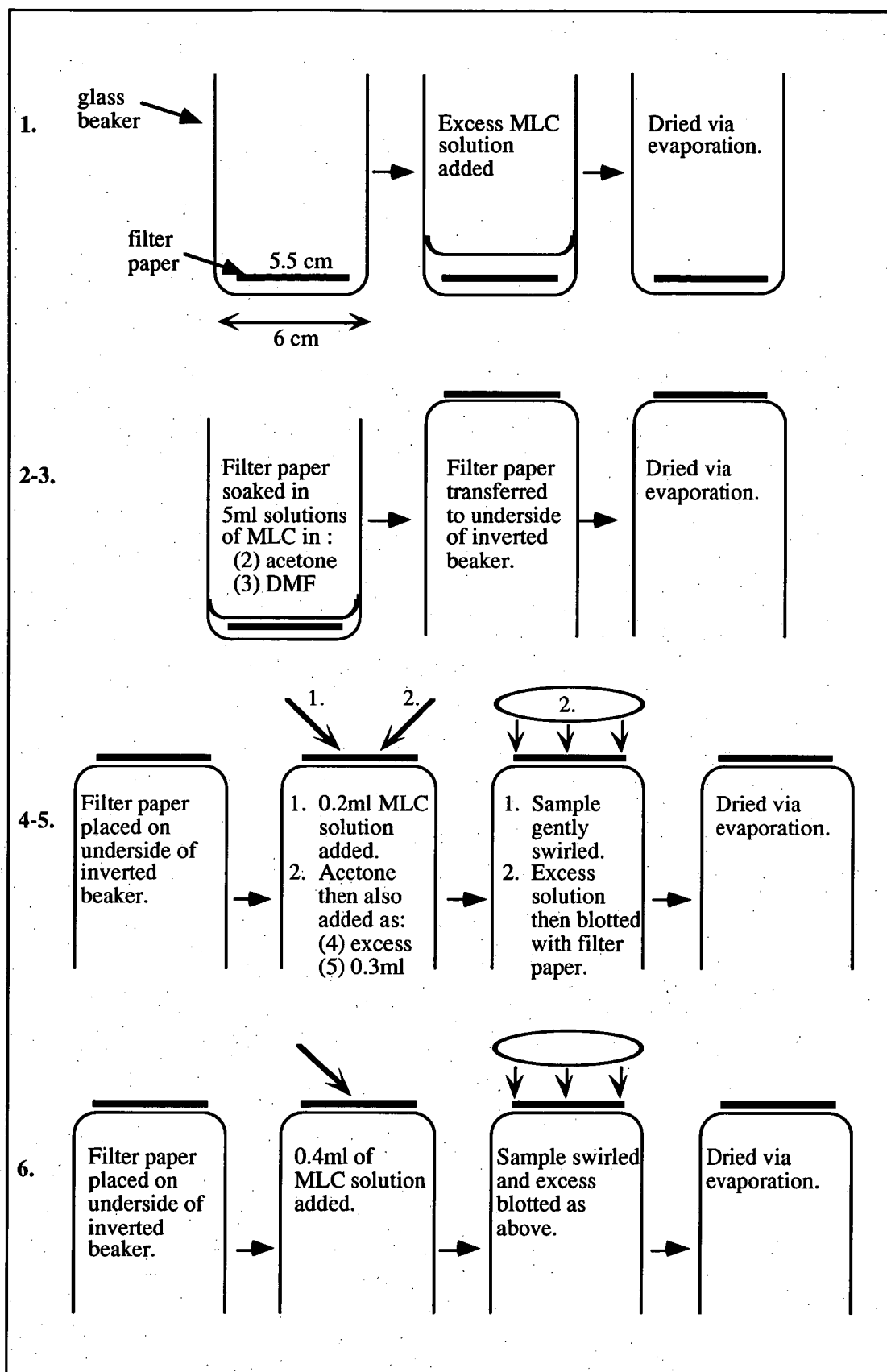
4. The filter paper was placed on the underside of an inverted beaker as in Method 2. 0.2ml of the sample was applied to the filter paper using a syringe. Excess acetone was then also added using a syringe, and the beaker swirled manually to spread the acetone evenly. The excess was blotted off with filter paper, and left to dry as with Method 2. Too much sample was lost in the excess acetone, giving a weak and therefore unreliable representation.

5. As with Method 4, but 0.3ml of acetone was added instead of excess acetone. This resulted in an even application, but coloured species in the sample may again have been lost with the acetone, as samples also appeared too pale.

6. 0.4ml of the sample was applied to filter paper on the underside of an inverted beaker, swirled, blotted and dried (overnight) as in Method 4. This provided a good even adsorption, with minimal loss of coloured species within the sample.

A schematic summary of these adsorption techniques is shown in Diagram 4.1.

Method 6 proved the most favourable sampling technique, and repeated measurements using the Elrepho datacolor 2000 gave consistent values. Thus Method 6 was used for sampling throughout all experiments involving MLCs in both this chapter and the following chapters. Percent loading of the sample onto the filter paper was calculated for this method and was  $1.5 \pm 0.7\%$  for all samples measured, including the solvent control. Therefore the DMF solvent in the MLC studies did not undergo complete evaporation, and thus the filter paper medium contained both adsorbed DMF solvent and substrate. (Note that this was in contrast to the complete evaporation found for the solvent used in Chapter 3 (acetone), leaving only substrate on TMP and BTMP handsheets).



**Diagram 4.1.** A schematic summary of different adsorption techniques explored for transferring MLC solutions evenly onto a solid medium.

### 4.3 Results and Discussion

Table 4.2 shows the colour changes observed for MLCs irradiated by the Ultravitalux sunlamps for 12 hours. The extent of reversion as revealed by the absorption coefficients ( $k$ ) and tristimulus colour parameters ( $L^*$ ,  $a^*$  and  $b^*$ ) is shown in Tables 4.3a and b. Included in these tables are the results for the solvent control, DMF.

The effect of irradiation on the MLCs as shown in the tables revealed five different kinds of responses, which were:

1. No changes in  $k$  or any tristimulus parameter, indicating that there was insignificant chromophore production and discolouration (for example 3-(4-methoxy)-1,2-propanediol).

2. An increase in  $k$  and  $b^*$ , a decrease in  $L^*$ , but no change in  $a^*$ , indicating that reversion had occurred with chromophore production, yellowing and darkening, but no changes in the red-green components of colour (for example guaiacol).

3. As with 2, but accompanied by a change in  $a^*$ , the red-green components of colour (for example methoxyhydroquinone).

4. Increases in  $k$  and  $b^*$ , a decrease in  $a^*$  accompanied by a change in sign from positive to slightly negative, but no significant change in  $L^*$  occurred for acetovanillone. These changes indicate that photo-reactions had occurred with production of chromophores, a simultaneous increase in yellowing and removal of red colouration, but darkening had not occurred.

5. A small decrease in  $L^*$  and  $a^*$ , and possibly a slight decrease in  $b^*$ , but no change in  $k$  was observed for 4-hydroxy-3-methoxy cinnamaldehyde. This indicates that a photo-reaction may have occurred, but no chromophores were formed and no yellowing took place.

The following discussions will follow these five categories. Where indicated, results will be drawn from Tables 4.3 and 4.4. Conclusions will also be supported with UV-visible absorption spectra and mass spectra data. Prior to discussing the results of the MLC studies, the solvent control will be discussed.

**Table 4.2.** Observed colours of MLC solutions before and after 12 hours of irradiation by Ultravitalux sunlamps.

Model lignin compound (MLC)	Observed colour of MLC in DMF solution.	
	0 hours	12 hours
Acetovanillone	pale yellow	bright yellow
Benzophenone	colourless	colourless
1,4-Benzoquinone	dark brown	dark reddish brown
Eugenol	colourless	pale yellow
Ferulic acid	pale yellow tinge	pale yellow tinge
Guaiacol	colourless	pale orange
4-Hydroxy-3-methoxy cinnamaldehyde	bright orange	orange
Isoeugenol	colourless	slight orange tinge
4-Methoxyacetophenone	colourless	colourless
Methoxyhydroquinone	orange - brown	orange - red
3-(4-Methoxyphenoxy)-1,2-propanediol	colourless	colourless
Methylhydroquinone	colourless	light orange - pink
(trans) Stilbene	colourless	colourless
Syringaldehyde	pale yellow tinge	light orange - yellow
Vanillic acid	colourless	light orange - yellow
Vanillin	colourless	light orange
Veratric acid	colourless	colourless
Solvent control, DMF	colourless	colourless



**Table 4.3a.** The absorption coefficients,  $k$  ( $\text{g/m}^2$ )<sup>-1</sup>, for MLCs before and after 12 hours of irradiation by Ultravitalux sunlamps.

Model lignin compound (MLC)	k 0 hours	k 12 hours	$\Delta k_{12-0 \text{ hours}}$
Acetovanillone	2.6	3.7	1.1
Benzophenone	0.8	0.8	0.0
1,4-Benzoquinone	$24.4 \pm 0.3$	$31.9 \pm 0.7$	$7.5 \pm 0.8$
Eugenol	0.9	1.5	0.6
Ferulic acid	1.0	1.1	0.1
Guaiacol	1.0	1.8	0.8
4-Hydroxy-3-methoxy cinnamaldehyde	4.4	4.5	0.1
Isoeugenol	1.2	1.7	0.5
4-Methoxyacetophenone	0.9	0.8	-0.1
Methoxyhydroquinone	$19.1 \pm 0.3$	$31.0 \pm 0.7$	$11.9 \pm 0.8$
3-(4-Methoxyphenoxy)-1,2-propanediol	0.8	0.8	0.0
Methylhydroquinone	1.4	5.1	3.7
(trans) Stilbene	0.9	0.9	0.0
Syringaldehyde	1.7	6.7	5.0
Vanillic acid	0.8	1.8	1.0
Vanillin	3.0	$8.2 \pm 0.4$	$5.2 \pm 0.4$
Veratric acid	0.7	0.8	0.1
Solvent control, DMF	0.8	0.8	0.0

Note that standard deviations are  $\pm 0.1$  unless stated otherwise.



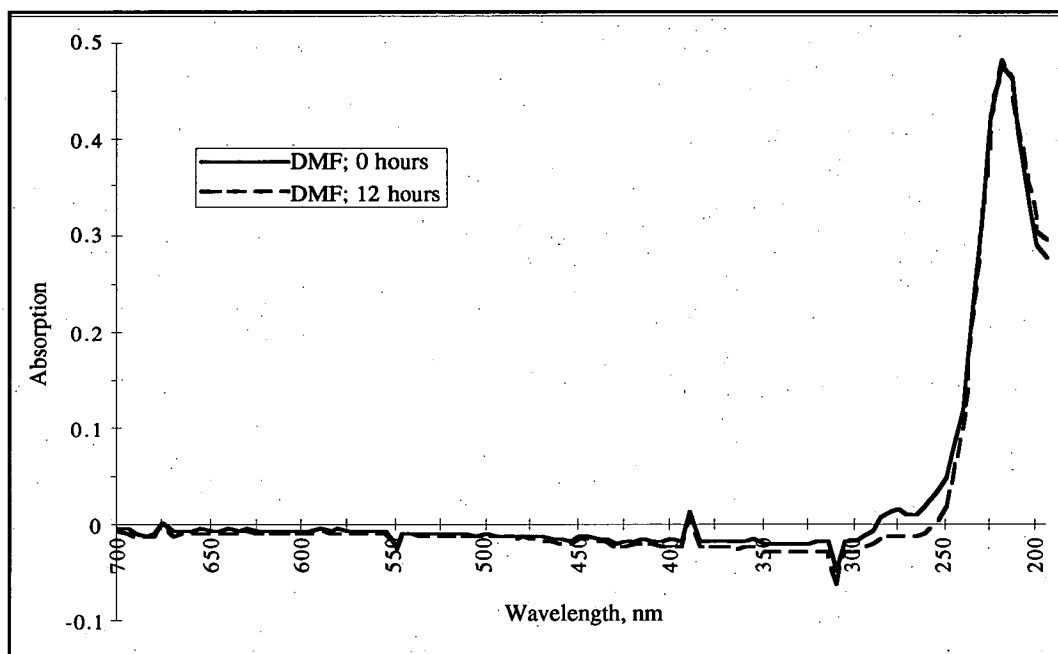
**Table 4.3b.** The tristimulus colour parameters  $L^*$ ,  $a^*$  and  $b^*$  for MLCs before irradiation and the changes in these parameters (irradiated - non-irradiated values) after 12 hours of irradiation by Ultravitalux sunlamps.

MLC	$L^*$	$\Delta L^*$	$a^*$	$\Delta a^*$	$b^*$	$\Delta b^*$
Acetovanillone	97.22	$0.06 \pm 0.03$	0.5	-0.7	2.5	1.5
Benzophenone	98.44	$-0.05 \pm 0.03$	-0.1	0.0	0.9	0.0
1,4-Benzoquinone	$89.96 \pm 0.03$	$-0.26 \pm 0.06$	5.9	-1.8	5.0	4.9
Eugenol	98.29	$-0.26 \pm 0.03$	0.1	-0.1	1.0	0.6
Ferulic acid	$98.29 \pm 0.03$	$-0.09 \pm 0.04$	-0.1	0.0	1.2	0.1
Guaiacol	98.18	$-0.41 \pm 0.03$	0.0	0.3	0.9	0.9
4-Hydroxy-3-methoxy cinnamaldehyde	97.93	$-0.30 \pm 0.03$	-2.2	0.9	6.9	-0.8
Isoeugenol	98.20	$-0.27 \pm 0.03$	-0.1	0.0	1.4	0.6
4-Methoxyacetophenone	98.33	$0.03 \pm 0.04$	0.0	0.0	1.0	-0.1
Methoxyhydroquinone	$92.24 \pm 0.05$	$-2.70 \pm 0.06$	3.1	2.3	7.5	1.5
3-(4-Methoxyphenoxy)-1,2-propanediol	98.40	$0.00 \pm 0.04$	-0.1	0.1	0.8	0.1
Methylhydroquinone	97.92	$-1.73 \pm 0.03$	0.2	1.1	1.3	2.3
(trans) Stilbene	98.35	$0.02 \pm 0.03$	-0.1	0.0	0.9	0.0
Syringaldehyde	97.91	$-0.99 \pm 0.03$	-0.1	-0.7	2.0	4.7
Vanillic acid	98.39	$-0.47 \pm 0.03$	-0.1	0.0	0.9	1.3
Vanillin	97.27	$-1.2 \pm 0.1$	-0.3	-0.1	3.2	$3.2 \pm 0.4$
Veratric acid	98.46	$-0.10 \pm 0.03$	-0.1	0.0	0.8	0.0
Solvent control, DMF	98.33	$-0.01 \pm 0.03$	-0.1	0.0	0.8	0.0

Note that standard deviations are  $\pm 0.02$  for  $L^*$  and  $\pm 0.1$  for  $a^*$  and  $b^*$  unless stated otherwise.

### 4.3.1 Solvent control, DMF

The solvent, DMF, underwent no changes in colour, the absorption coefficient,  $k$ , or any of the tristimulus colour parameters shown in Tables 4.2 and 4.3. Its diffuse reflectance UV-visible absorption spectra before and after irradiation is shown in Figure 4.4. As no significant changes were observed between these two spectra it can be assumed that the DMF solvent has undergone no photo-induced reaction.



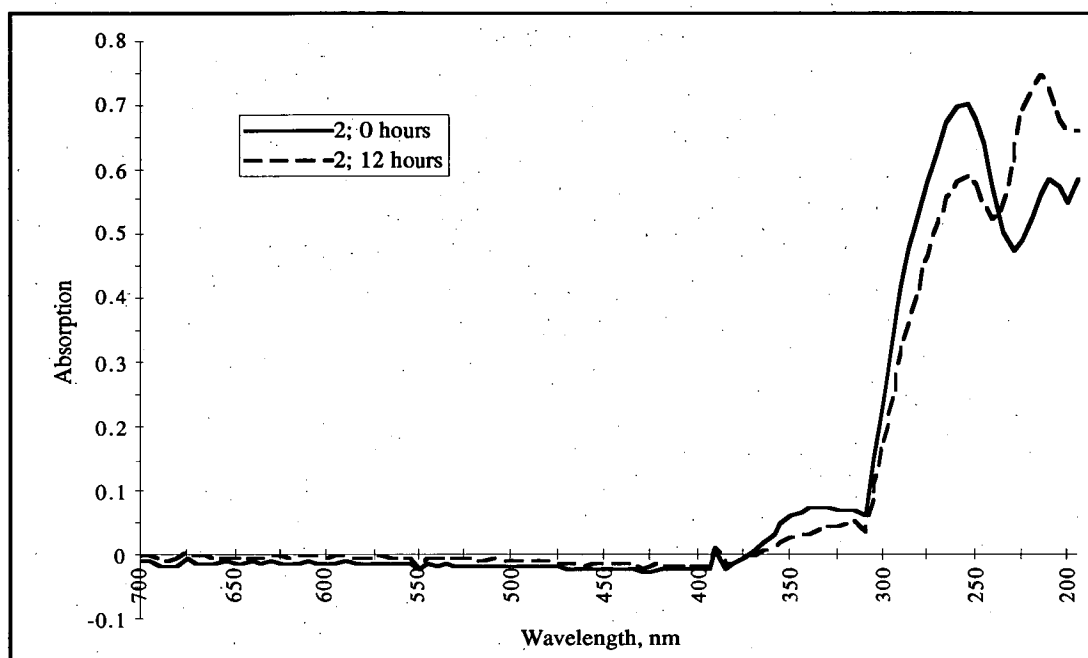
**Figure 4.4.** UV-visible absorption spectra for the solvent DMF before and after 12 hours of irradiation by Ultravitalux sunlamps.

The UV cut off of DMF at 270nm was discussed in Section 4.2.4, posing a problem of interference for solution UV-visible absorption spectra. Figure 4.4 revealed DMF to have two peaks in the solid diffuse reflectance spectra, a relatively sharp peak at 220nm and a small peak at 280nm. Naturally these peaks must be considered in the spectra of the MLCs, but they certainly do not cloud a large spectral region, and so interference by the solvent is not a big problem for the solid state spectra.

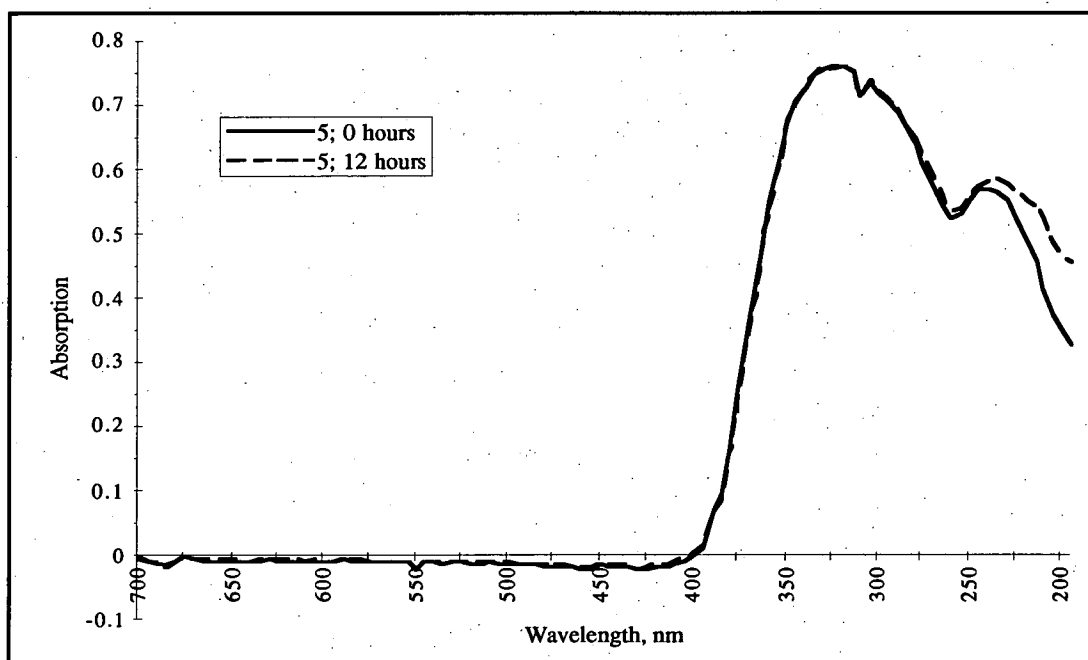
### 4.3.2 Category 1 compounds: Insignificant reversion detected

Compounds which belonged to this category were benzophenone (2), ferulic acid (5), 4-methoxyacetophenone (9), 3-(4-methoxyphenoxy)-1,2-propanediol (11), *trans* stilbene (13) and veratric acid (17). Interestingly, none of these compounds, except for ferulic acid, contained a phenolic hydroxyl group. This supports the proposal

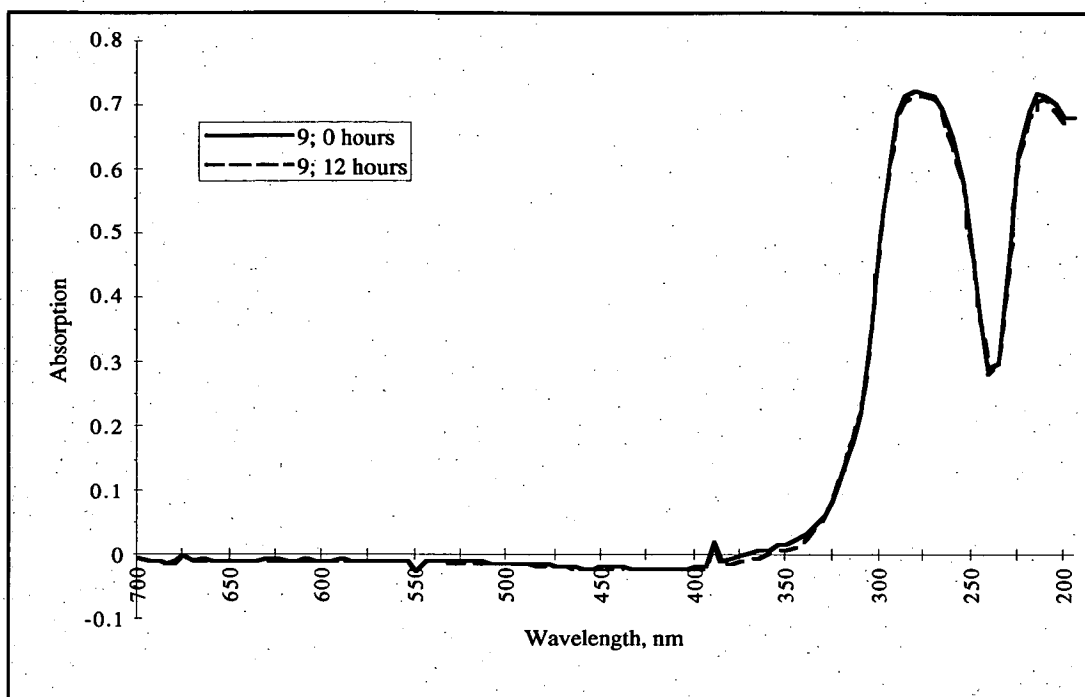
introduced in Section 1.2 that the phenolic hydroxyl group plays an important role in many photo-yellowing reactions. Most of these Category 1 compounds did, however, contain possible photo-sensitiser groups (2, 5, 9, 13 and 17), and some had these groups in conjunction with other functional groups (5, 9 and 17). There is a possibility, therefore, that these types of compounds may act as photo-sensitiser groups without yellowing themselves. This will be discussed further below, along with discussions of the UV-visible absorption spectra for these compounds before and after irradiation, which are shown in Figures 4.5-4.10.



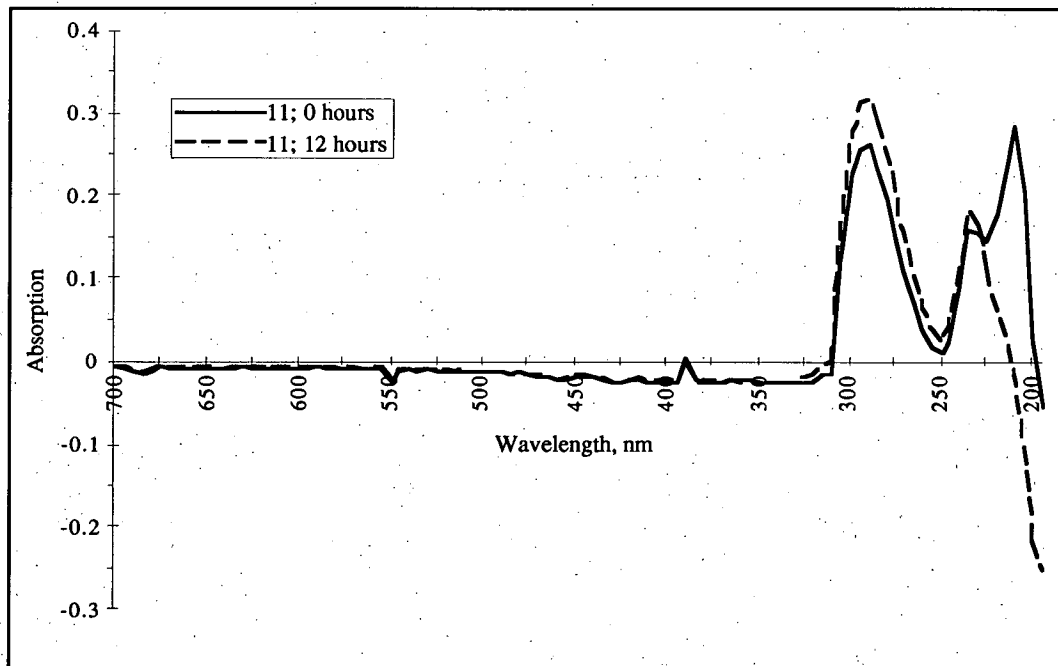
**Figure 4.5.** UV-visible absorption spectra for benzophenone before and after 12 hours of irradiation by Ultravitalux sunlamps.



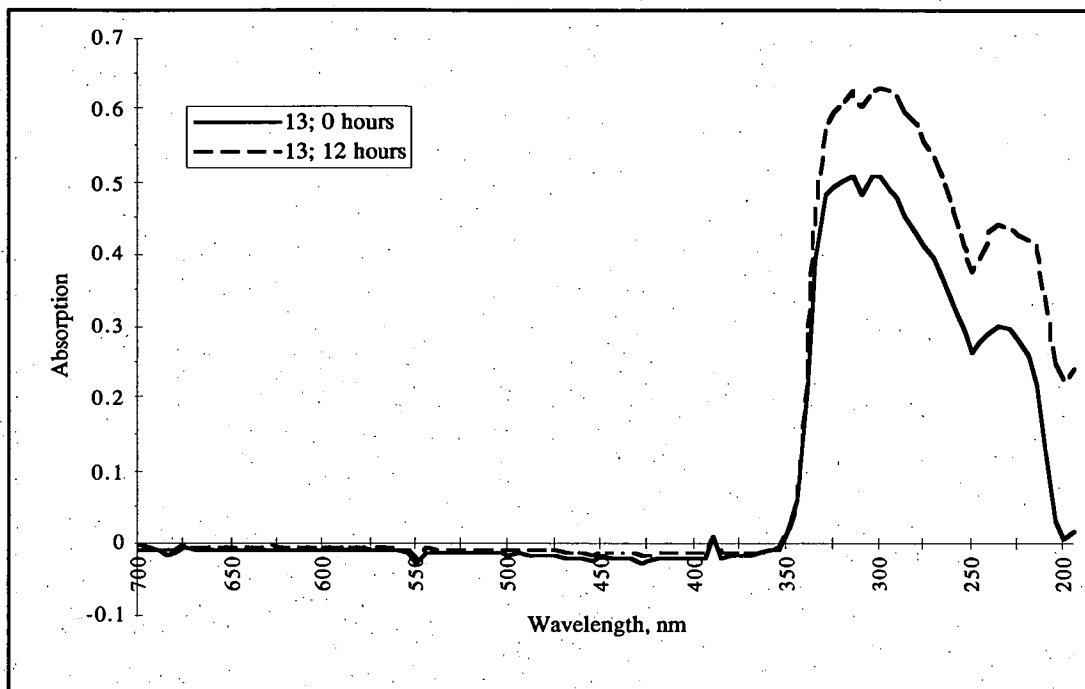
**Figure 4.6.** UV-visible absorption spectra for ferulic acid before and after 12 hours of irradiation by Ultravitalux sunlamps.



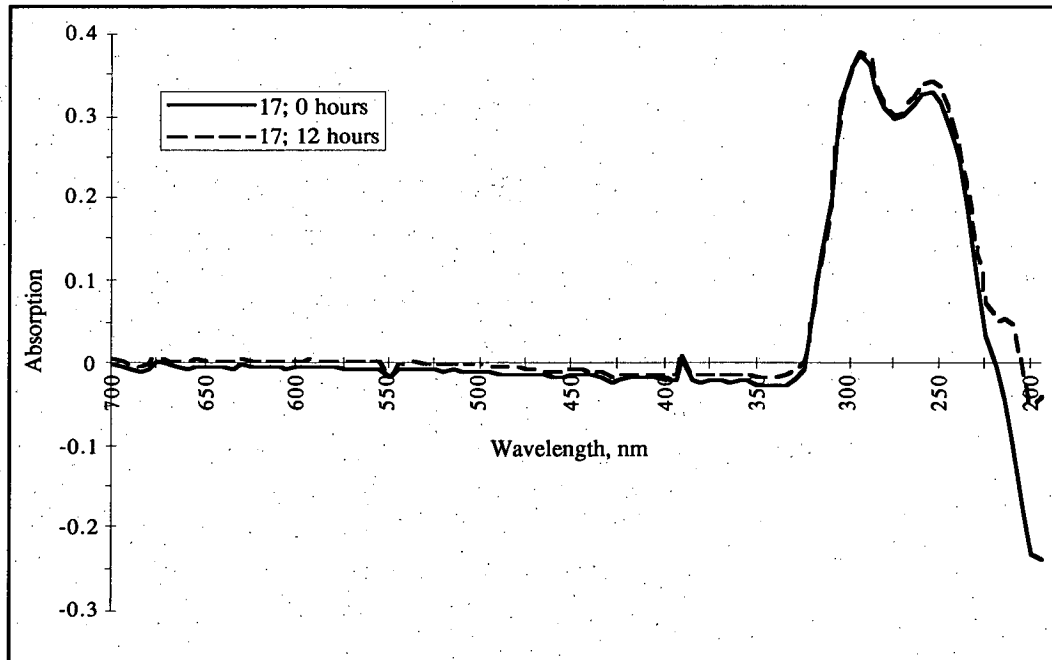
**Figure 4.7.** UV-visible absorption spectra for 4-methoxyacetophenone before and after 12 hours of irradiation by Ultravitalux sunlamps.



**Figure 4.8.** UV-visible absorption spectra for 3-(4-methoxyphenoxy)-1,2-propanediol before and after 12 hours of irradiation by Ultravitalux sunlamps.



**Figure 4.9.** UV-visible absorption spectra for *trans* stilbene before and after 12 hours of irradiation by Ultravitalux sunlamps.



**Figure 4.10.** UV-visible absorption spectra for veratric acid before and after 12 hours of irradiation by Ultravitalux sunlamps.

#### **4-Methoxyacetophenone**

The spectra for 4-methoxyacetophenone prior to and after irradiation were identical (Figure 4.7), therefore this compound did not undergo any structurally altering chemical changes.

#### **Carboxylic acids: Ferulic acid and veratric acid**

The spectra before and after irradiation for the two carboxylic acids in this group (ferulic acid (Figure 4.6) and veratric acid (Figure 4.10)) were also identical, except for a small hyperchromic effect (i.e. increase in intensity) at 210nm. This could be due to some photo-activity of the carboxyl group, which has a  $\nu_{\max}$  in this region. Surprisingly, the well known isomerisation of *trans* to *cis* ferulic acid under the influence of UV light did not appear to have occurred under the experimental conditions used. Such an isomerisation should have resulted in the spectrum after irradiation in Figure 4.6 to have been reduced in intensity with respect to the non-irradiated spectrum (as the absorption coefficients,  $E_{\max}$ , for *cis* ferulic acid are approximately half those of *trans* ferulic acid).

Ferulic acid was the only compound belonging to this group that contained a phenolic hydroxyl group. It could be that the photo-activity at the  $\gamma$ -carboxyl group may have shielded photo-activity about the  $C_{\alpha}=C_{\beta}$  photo-sensitising group, or shielded other photo-yellowing reactions. This possibility will be discussed in further detail later in this chapter as the results of other carboxylic acid compounds are revealed.

#### **Benzophenone**

Although insignificant reversion was indicated by the colour parameters for benzophenone (see Tables 4.2 and 4.3), its UV-visible absorption spectra before and after irradiation were quite different (see Figure 4.5). The spectrum for benzophenone revealed three absorption peaks, at 340, 255 and 210nm. Irradiation resulted in hypochromic effects (i.e. decreases in intensity) in the peaks at 340nm and 255nm, suggesting that some photo-activity had occurred. A hyperchromic effect was apparent in the peak at 210nm, which may also have undergone a small bathochromic (or red) shift to 215nm. This is also indicative of the occurrence of some photo-induced change. This peak, however, corresponds to the region of intense absorption seen in Figure 4.4 for the solvent, DMF. Despite no changes in this peak being observed on irradiation for DMF alone, the amount of interference by the DMF peak is uncertain, and therefore conclusions must be taken lightly. A small

decrease in absorption at 195nm was also apparent after irradiation. Carbonyl groups absorb at 190nm, so this decrease in absorption could indicate some photo-activity about the carbonyl group of benzophenone. As this occurs at the lower limit of the spectrophotometer's range, however, it could be erroneous. There could also have been a small decrease in a shouldering peak at 280nm, but again this is unclear due to the broadness of the 250nm peak. Nonetheless, it appears that benzophenone has undergone some photo-reaction. This is not surprising as benzophenone has indeed been used as a photo-initiator in many photo-polymerisation reactions<sup>115</sup>.

### ***3-(4-methoxyphenoxy)-1,2-propanediol***

For 3-(4-methoxyphenoxy)-1,2-propanediol, (Figure 4.8), a peak at 210nm was almost completely removed by irradiation. Again, the extent of interference by the solvent peak in this region is unclear, but the result still indicates that a photo-reaction, which did not lead to the production of coloured species, had occurred.

### ***trans Stilbene***

*trans* Stilbene contained similarly positioned peaks before and after irradiation, (Figure 4.9), but a hyperchromic effect was observed for each peak after irradiation. Thus it is possible that some photo-activity may have occurred for this compound as well, but no structurally altering reaction. It should be noted that the lack of photo-discolouration observed for stilbene contradicts results of studies by several authors, who found stilbenes to undergo strong photo-yellowing<sup>70,114</sup>. (This was, in fact, stated in Section 1.4 as one of the reasons for the inclusion of *trans* stilbene in this study). This contradiction is easily explained, however, as each stilbene investigated in the literature was substituted, containing at least one phenolic-hydroxyl group, whereas the stilbene used in the current study was unsubstituted. This comparison further highlights the importance of a phenolic hydroxyl group for photo-yellowing to occur.

### ***Summary for Category 1 compounds***

In general, the lack of photo-yellowing observed by compounds belonging to this category can be attributed to the absence of a phenolic hydroxyl group. The exception to this was ferulic acid, which did contain a phenolic hydroxyl group. It is possible that in this case, the presence of a COOH end group, in conjugation with a C $\alpha$ =C $\beta$  bond of a 3-carbon side chain, has interfered with photo-yellowing reactions.

Despite no photo-yellowing observed for compounds in this category, the UV-visible absorption spectra revealed photo-activity had still occurred in some cases, particularly for benzophenone, 3-(4-methoxyphenoxy)-1,2-propanediol, *trans* stilbene, and possibly for the two carboxylic acids in this category (veratric acid and ferulic acid). Each of these compounds contained a potential photo-sensitiser group, which could possibly sensitise or indirectly contribute to photo-yellowing reactions in a complex system like lignin.

#### **4.3.3 Category 2 compounds: Reversion with no change in the red-green colour coordinate $a^*$**

Significant reversion, with an increase in the chromophore concentration, associated yellowing and darkening, but no detectable change in the red-green colour coordinate  $a^*$ , (as presented in Tables 4.3a and b), was shown for eugenol (4), guaiacol (6), isoeugenol (8), vanillic acid (15) and vanillin (16). All of these compounds, except for guaiacol, contained a possible sensitiser group (C=O, or C=C), phenolic hydroxyl, and methoxyl groups. Guaiacol contained a phenolic hydroxyl and methoxyl group only.

These compounds will be discussed separately below, along with discussions of their UV-visible absorption spectra before and after irradiation, and mass spectra after irradiation. Before proceeding, it should be noted that fragments detected in the mass spectra of lower molecular weights than the starting material, (referred simply as "lower molecular weight" fragments in the following discussions), could have been introduced by ionisation procedures within the mass spectrometer itself. Therefore, discussions centering around such fragments are of consideration only and are not to be taken as conclusive evidence.

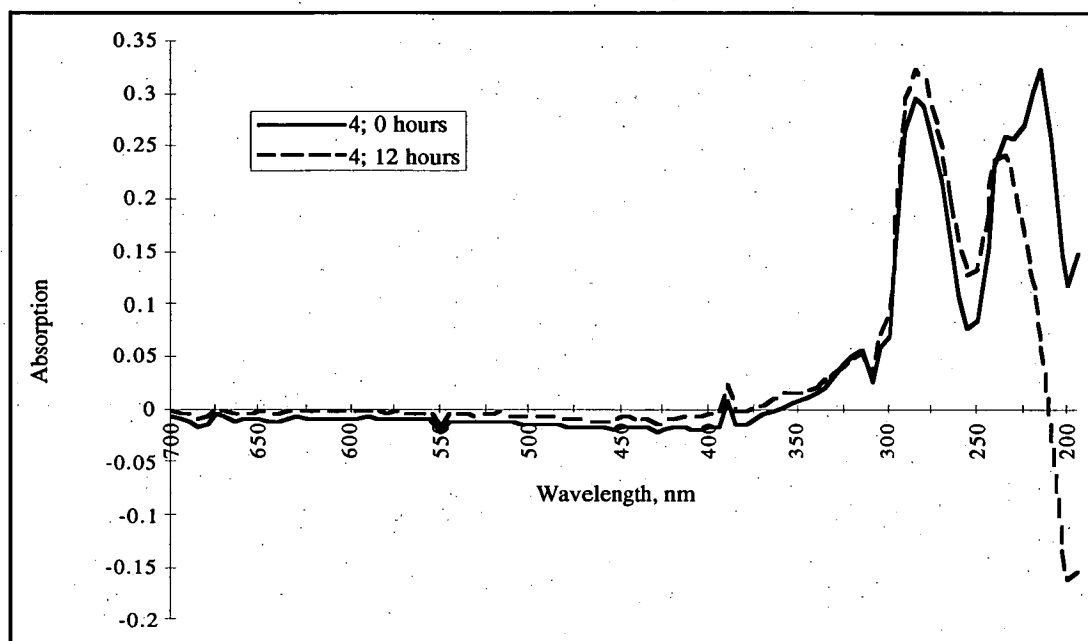
##### ***Eugenol***

The UV-visible absorption spectra for eugenol before and after irradiation are shown in Figure 4.11, and its mass spectra after irradiation is presented in Appendix A.

The UV-visible absorption spectra revealed a small hyperchromic effect at 285nm for eugenol on irradiation, along with a depletion of absorption between 205 and 215nm. This latter change could be indicative of photo-activity about the C=C bonds of eugenol, as these groups absorb at approximately 195nm. This is difficult to interpret accurately, though, as this region is close to the large absorption found for the DMF solvent (see Figure 4.4), and is also close to the lower spectral limit of the spectrophotometer, and therefore subject to larger error fluctuations. A very small increase in absorption at about 360nm could be due to the formation of quinone



species ( $\nu_{\max}$  of 365-367nm<sup>59</sup>), but this was very weak and close to the baseline, so could alternatively have been due to noise interference.



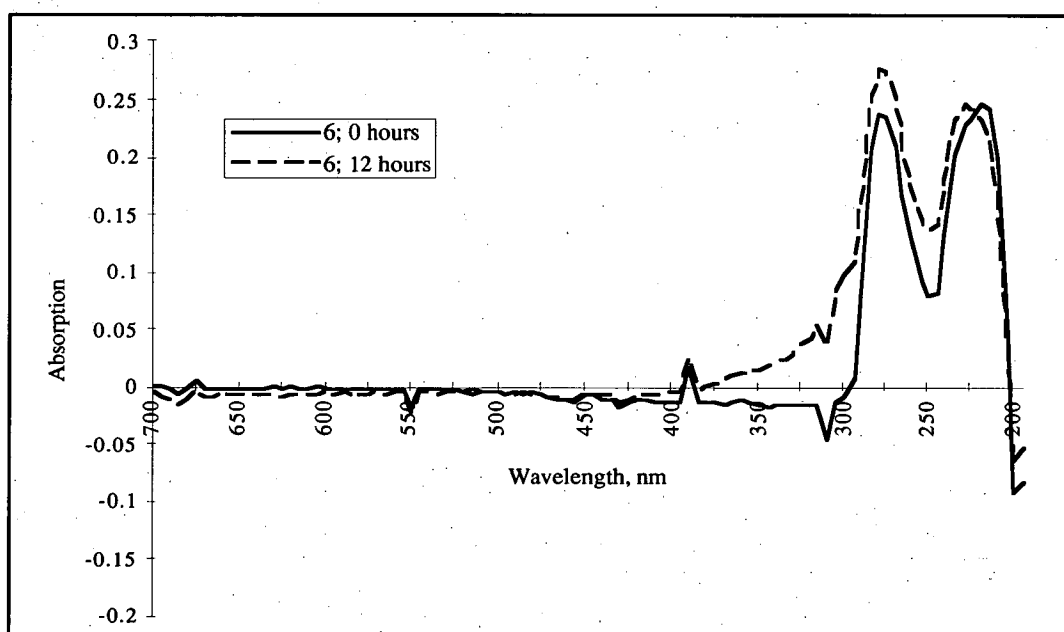
**Figure 4.11.** UV-visible absorption spectra for eugenol before and after 12 hours of irradiation by Ultravitalux sunlamps.

The mass spectra for irradiated eugenol (see Appendix A), detected the presence of eugenol dimers/oligomers (M.W. 326) as products of irradiation. It also detected a fragment of molecular weight equivalent to the corresponding quinone species of eugenol (M.W. 148). As mentioned above, such a fragment may have been introduced by ionisation of eugenol in the mass spectrometer itself, but when coupled with the possible absorption found at 360nm in Figure 4.11, its presence strengthens the argument that eugenol may have been converted to quinones upon irradiation. Other low molecular weight fragments detected in the mass spectra included species corresponding to eugenol minus a methyl ( $\text{CH}_3$ ) group (M.W. 149), and eugenol minus a methoxyl ( $\text{OCH}_3$ ) group (M.W. 133). Demethylation<sup>4,7</sup> and demethoxylation<sup>4,7,44,50</sup> have been shown to occur during the irradiation of lignin, so it is possible that eugenol may also have undergone a photo-induced cleavage of these groups.

In conclusion, the results revealed that eugenol underwent dimerisation upon irradiation. Other photo-reactions may also have occurred, including photo-induced cleavages (i.e. demethylation and demethoxylation), and conversion of eugenol to quinone species.

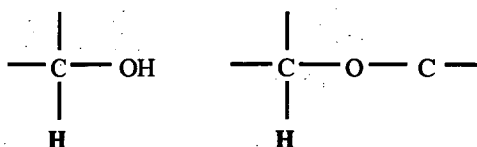
## Guaiacol

The UV-visible absorption spectra for guaiacol (Figure 4.12) revealed the introduction of a broad peak between 300 and 420nm upon irradiation. This can be attributed to the formation of coloured species, as it is nearing the visible region of the spectrum. It is likely that these species were quinones, which absorb typically in this region. The absorption spectra also revealed a small hypochromic effect at 215nm and hyperchromic effects at 230 and 280nm upon irradiation. Carbonyl groups absorb around 280nm, so the hyperchromic effect in this region could indicate a formation of C=O groups after irradiation. This does not explain the initial presence of a peak in this region, however, as guaiacol does not contain a carbonyl group.

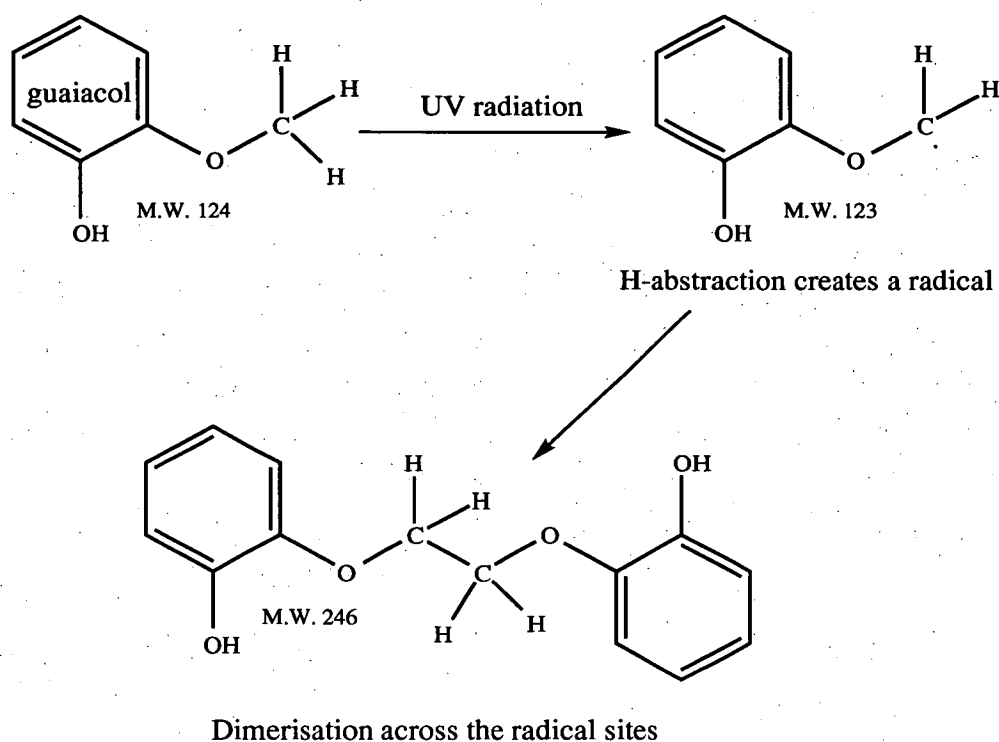


**Figure 4.12.** UV-visible absorption spectra for guaiacol before and after 12 hours of irradiation by Ultravitalux sunlamps.

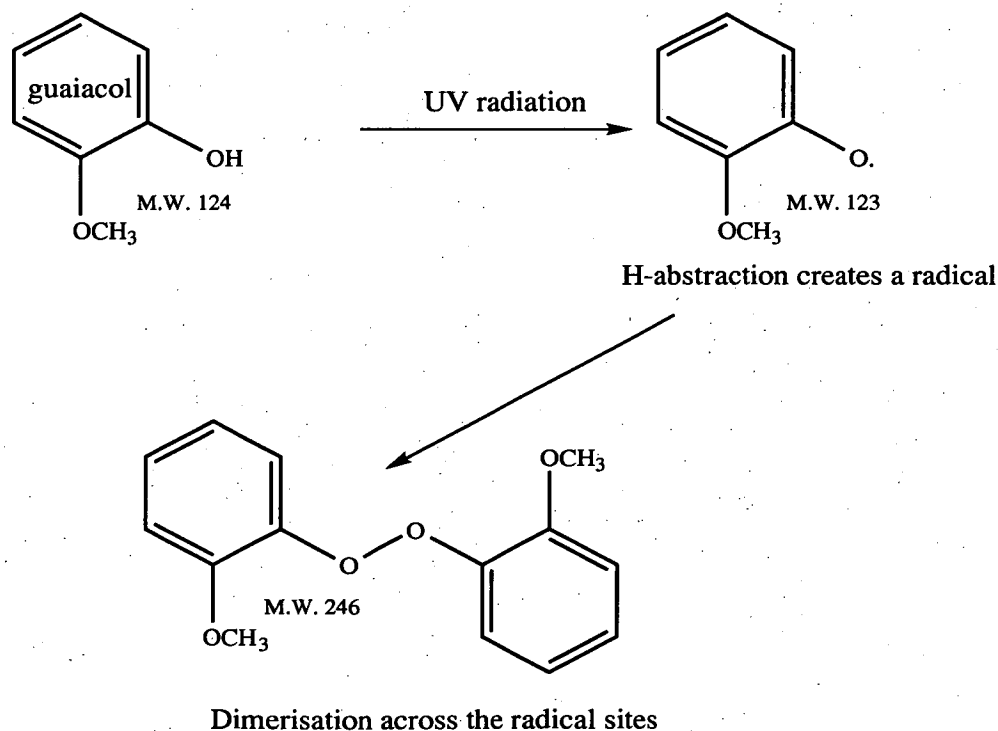
The mass spectra for irradiated guaiacol (see Appendix A) revealed the presence of dimers minus 2 hydrogen atoms (MW 246) and trimers minus 4 hydrogen atoms (MW 368). This possibly occurred via photo-induced H-abstraction, forming guaiacyl radicals which then combined to form the dimers and trimers. It is common for compounds containing alcohol or ether groups to undergo photo-induced abstraction of the adjacent hydrogen in the *ipso*-position<sup>115</sup>, i.e.



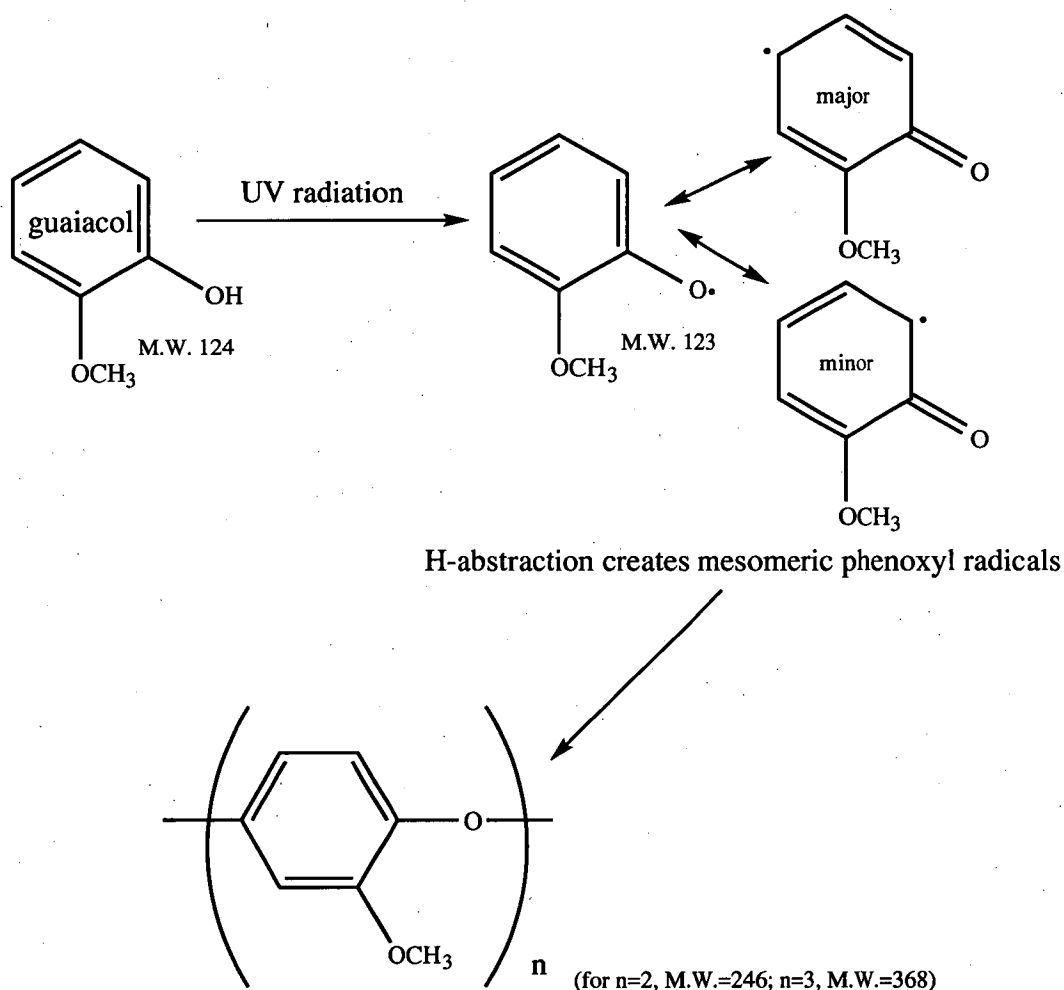
This would suggest the following reaction scheme as a possibility for the H-abstraction and subsequent dimerisation of guaiacol:



The above reaction scheme precludes the phenolic hydroxyl group from playing any significant role. The phenolic hydroxyl group, however, does appear to be significant in photo-yellowing reactions, as introduced in Section 1.2 and discussed further for the Category 1 compounds. It cannot be discounted, therefore, that the H-abstraction may have occurred at the phenolic hydroxyl group, with subsequent radical formation and dimerisation following the reaction scheme shown below:

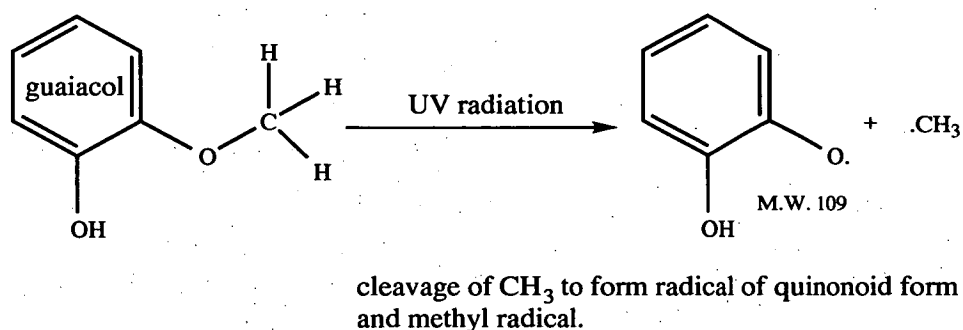


The above reaction mechanism suggests the formation of an organic peroxide compound as the resultant dimer. Although this could possibly have occurred, the resultant peroxide would be highly unstable and thus unlikely to have remained for a sufficient time period to be detected. It is most likely, therefore, that abstraction of the phenolic hydrogen resulted in the formation of mesomeric phenoxyl radicals, which in turn coupled with each other through C-O and C-C coupling modes to give oligomers. Such oligomers are supported by the mass spectra shown in Appendix A, as compounds with M.W. 246 and 368 were detected, which correspond to oligomers where  $n = 2$  and  $3$ , respectively. This is shown in the reaction scheme below:



A peak at MW 109 was also observed in the mass spectra for irradiated guaiacol (see Appendix A). This could represent the analogous quinone species of guaiacol (i.e. *o*-quinone, M.W. 108), in an ionised form. It also corresponds to guaiacol minus a  $\text{CH}_3$  fragment. This peak may have just resulted from ionisation steps in the mass spectrometer itself, but the possibility of it being a result of further irradiation products cannot be discounted, as demethylation has been shown to occur during the irradiation of lignin<sup>4,7</sup>. Removal of a  $\text{CH}_3$  fragment from the methoxyl group of

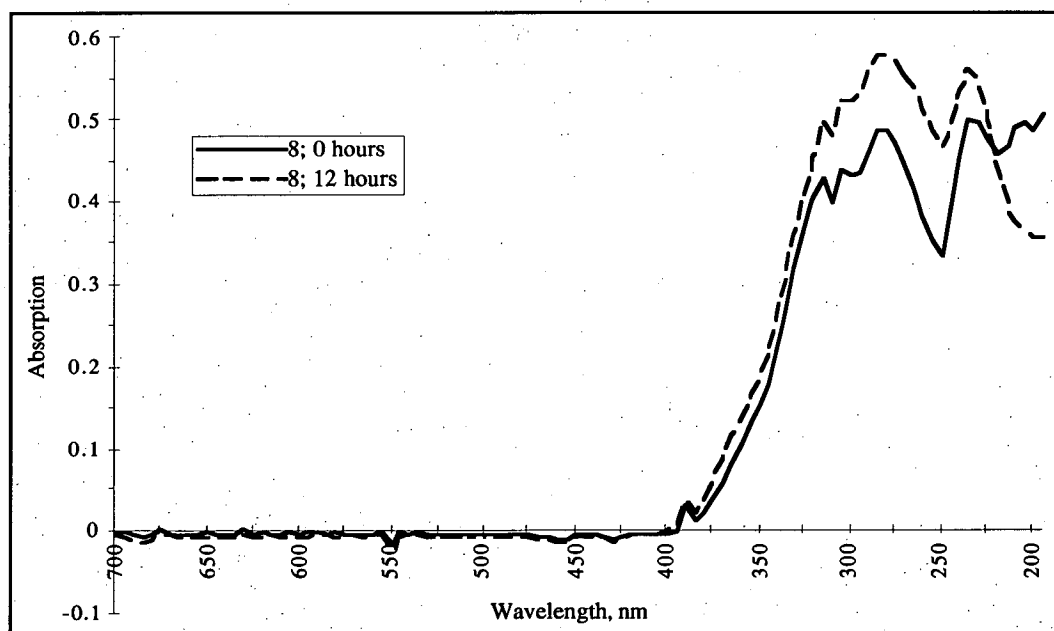
guaiacol could lead to the formation of a C=O group at this position. It could also result in the formation of a quinonoid radical, as shown below:



Thus it is possible that quinone species were not only a product of irradiated guaiacol, but may also have been involved as radical-intermediates in the photo-reactions of guaiacol.

### *Isoeugenol*

Although the UV-visible absorption spectra for isoeugenol (Figure 4.13) did not experience an introduction of absorption beyond 300nm after irradiation, it did experience a hyperchromic effect (i.e. increase in absorption) at 310nm. Hyperchromic effects were also observed at 235 and 285nm, while absorption at approximately 205-215nm was depleted on irradiation. This latter change could be indicative of photo-activity about the C=C bond of isoeugenol, as such groups absorb at approximately 195nm. As mentioned above for eugenol, however, this is difficult to interpret accurately as this region is close to the large absorption found for the DMF solvent, and is also close to the spectral limit of the spectrophotometer.



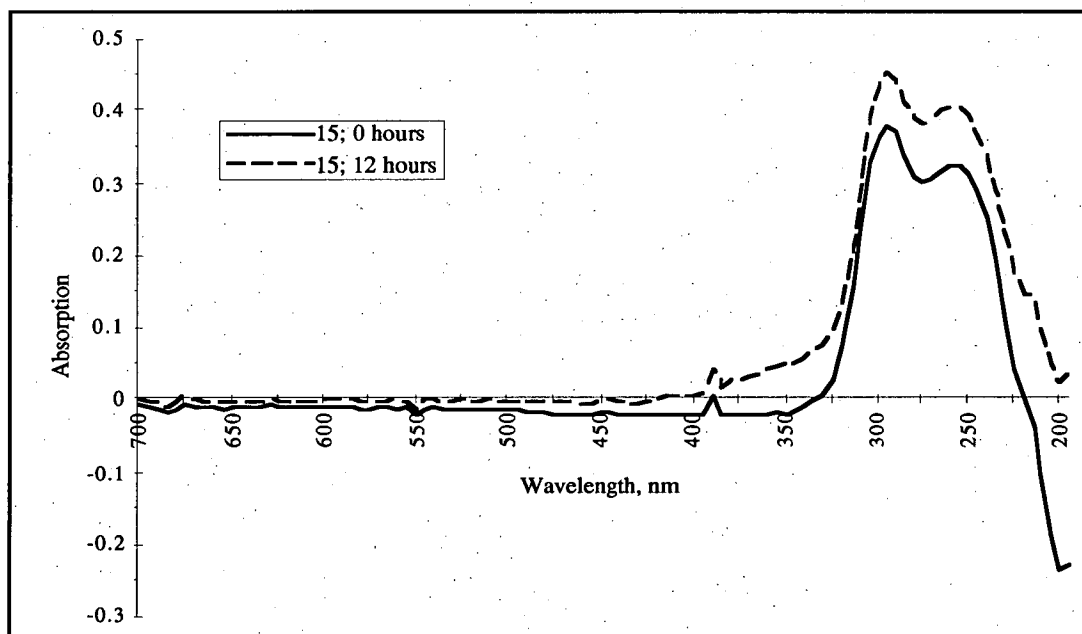
**Figure 4.13.** UV-visible absorption spectra for isoeugenol before and after 12 hours of irradiation by Ultravitalux sunlamps.

The mass spectra for irradiated isoeugenol, (see Appendix A), revealed the formation of dimeric structures on irradiation (with MW of 326), possibly via H-abstraction and oligomerisation steps, as discussed above for guaiacol. Several lower molecular weight fragments were also apparent in the mass spectra, including fragments with molecular weights corresponding to a demethoxylation (M.W. 133), and a demethylation of isoeugenol (or a quinone-like species, M.W. 149), similar to those discussed above for guaiacol.

Thus for isoeugenol, photo-reactions included oligomerisation, and may have included demethylation or production of quinone-like species or intermediates.

### *Vanillic acid*

The UV-visible absorption spectra for vanillic acid, (see Figure 4.14), upon irradiation revealed the formation of a broad peak at 360nm, which could indicate the formation of quinone species. As well as this, the absorption spectra also experienced hyperchromic effects in all of its other absorption peaks. Included in this was an increase in absorption of a shoulder at 215nm. This could indicate photo-activity at the COOH group, as it is near the region of  $\nu_{\text{max}}$  for this group.



**Figure 4.14.** UV-visible absorption spectra for vanillic acid before and after 12 hours of irradiation by Ultravitalux sunlamps.

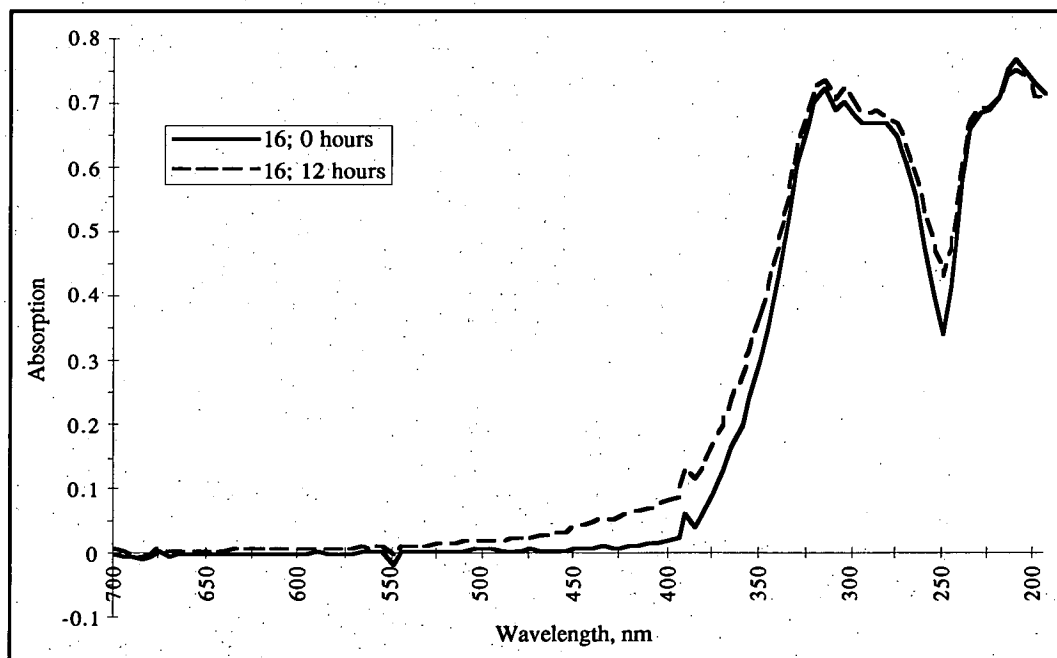
Ferulic acid and veratric acid, previously discussed as a Category 1 compounds, also contained possible photo-activity about their COOH groups, but neither of these compounds underwent any discolouration. The primary difference between vanillic

acid and veratric acid is that while vanillic acid contains a phenolic hydroxyl group, veratric acid does not. This re-affirms the importance of a phenolic hydroxyl group for photo-yellowing reactions to occur. For vanillic acid, the carboxyl group may have become excited, and initiated further photo-yellowing reactions centred about the phenolic hydroxyl group. Ferulic acid also contains both a carboxylic acid group and phenolic hydroxyl group, but the carboxyl group was not ring substituted like it was in vanillic acid. Instead it was positioned at the end of a 3-carbon side chain (i.e. in the gamma position). Therefore, it is possible that the positioning of the carboxyl group is also important for photo-yellowing to occur.

Unlike the Category 2 MLCs discussed so far, the mass spectra for irradiated vanillic acid (see Appendix A) revealed no oligomeric structures. The involvement of carboxylic acid groups in the photo-yellowing processes may induce different reaction pathways and products than for compounds which lack this group. A lower molecular weight fragment of M.W. 153 was present in the mass spectra for irradiated vanillic acid, which corresponds to vanillic acid minus a CH<sub>3</sub> group. This could indicate a demethylation process, or the involvement of a quinone-like species as shown for guaiacol above. Once again this is unconfirmed, however, as this fragment could also have been produced via ionisation and fragmentation in the mass spectrometer itself.

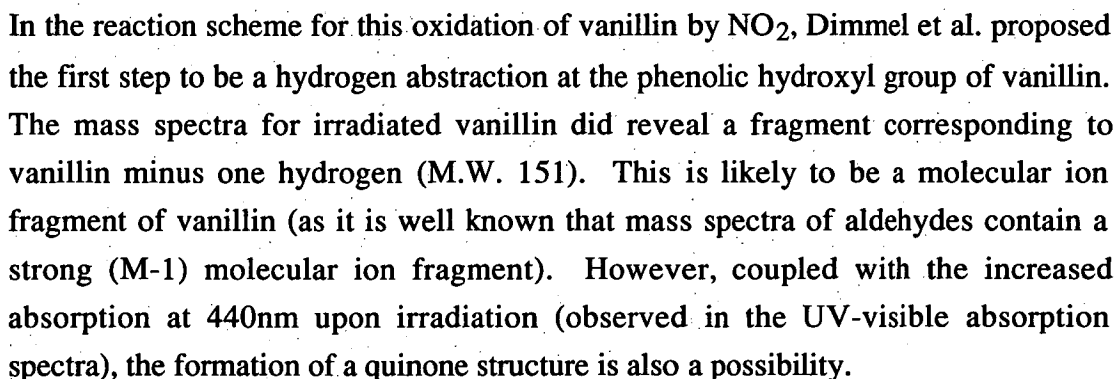
### Vanillin

The UV-visible absorption spectra before and after irradiation of vanillin are shown in Figure 4.11, and its mass spectra after irradiation is presented in Appendix A.



**Figure 4.15.** UV-visible absorption spectra for vanillin before and after 12 hours of irradiation by Ultravitalux sunlamps.

The mass spectra for irradiated vanillin detected a lower molecular weight fragment of M.W. 137. This could be indicative of a demethoxylation process (either during irradiation or ionisation in the mass spectrometer), or it could have been due to the formation of the corresponding benzoquinone species, methoxy-*p*-benzoquinone, which has M.W. 138. This species has been shown by Dimmel et al<sup>116</sup> to be produced in small quantities on oxidation of vanillin, using NO<sub>2</sub> as the oxidising agent. This is shown below:





The mass spectra for irradiated vanillin also detected a lower molecular weight fragment of M.W. 123, which corresponds to vanillin minus its aldehyde (CHO) group. This is equivalent to guaiacol which, being colourless, would not be expected to contribute to yellowing. It could, however, represent an intermediate in the yellowing process. The presence of a dimeric structure minus two hydrogen atoms (MW 302) was also detected in the mass spectra, so oligomerisation could also have occurred for vanillin via photo-induced H-abstractions, as discussed for guaiacol above.

### *Summary for Category 2 compounds*

Except for vanillic acid, all compounds belonging to "Category 2" formed dimeric structures upon irradiation, while guaiacol also produced a trimeric structure. This possibly occurred via photo-induced H-abstractions, forming radicals which could then have combined to form oligomers.

Evidence also supported the presence of a quinonoid species in each irradiated sample. This species could have been a radical intermediate, or a product of irradiation.

It is possible that all the compounds in this category, except for vanillin, may also have undergone a cleavage of CH<sub>3</sub> groups (demethylation). This may have led to the production of their corresponding quinonoid species or radicals.

Eugenol and vanillin may have undergone a cleavage of OCH<sub>3</sub> groups (demethoxylation) on irradiation, which could have led to the production of their corresponding quinone species.

Vanillic acid was the only compound in this category which contained a carboxylic acid group. As it was the only compound for which a dimeric structure was not detected as a reaction product, it is possible that the COOH group exerts a different photo-reactive action than other potential photosensitising groups.

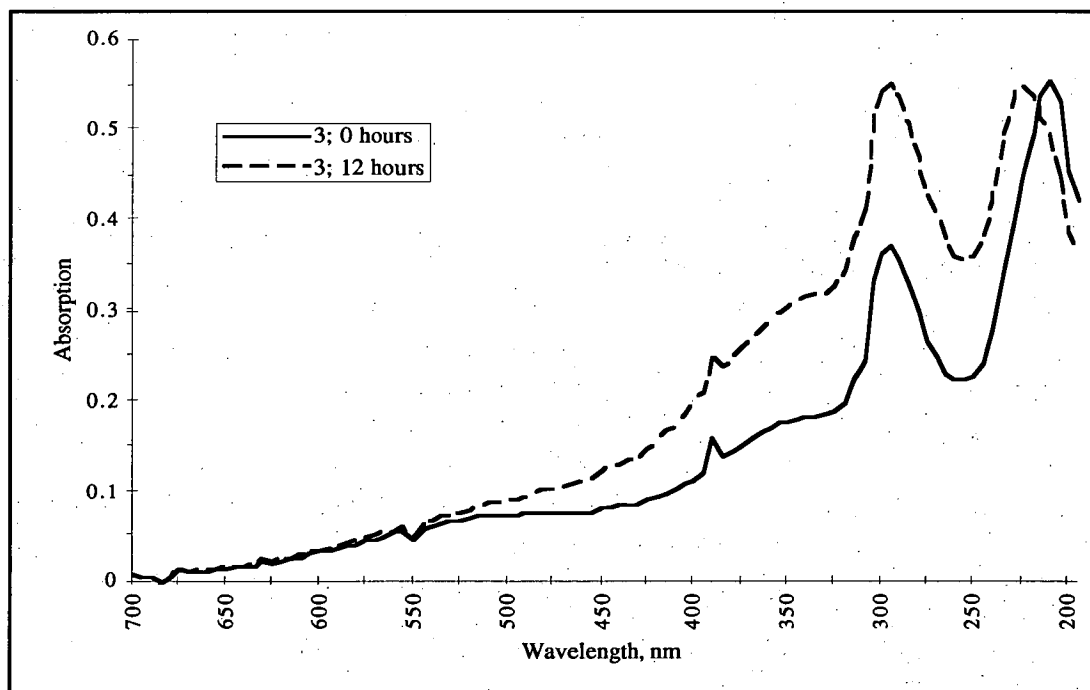
Comparing the photo-yellowing response of vanillic acid with the lack of yellowing found for ferulic acid, it appears that the positioning of the COOH group may determine whether or not yellowing will occur.

#### 4.3.4 Category 3 compounds: Reversion with a change in the red-green colour coordinate $a^*$

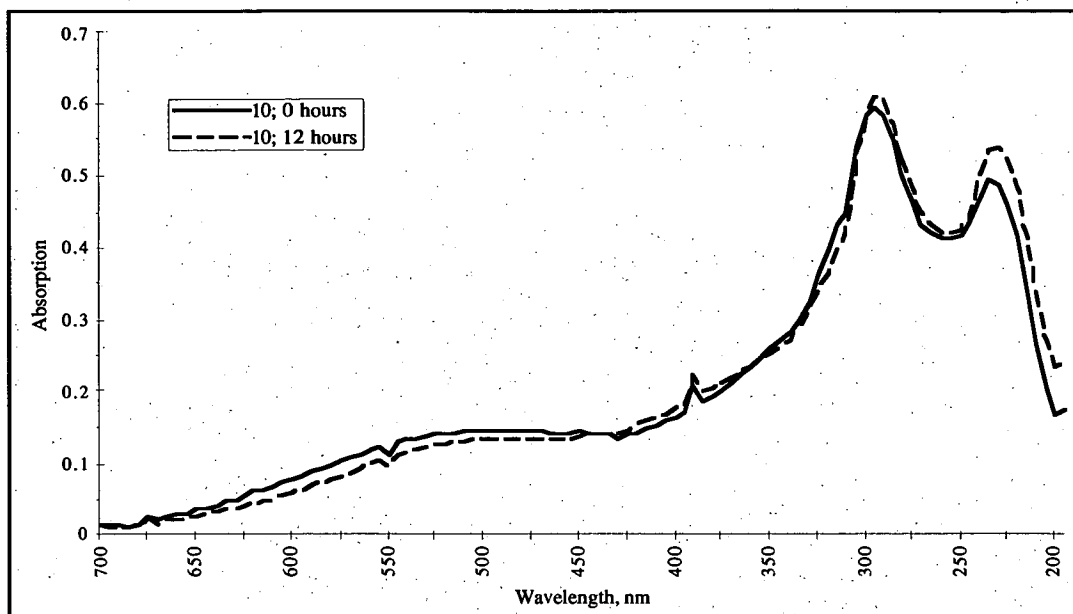
Reversion as indicated by an increase in chromophore content (increase in  $k$ ), yellowing (increase in  $b^*$ ), associated darkening (decrease in  $L^*$ ) and a change in the red-green colour parameter,  $a^*$ , occurred for the quinonoid species (benzoquinone (3), methoxyhydroquinone (10) and methylhydroquinone (12)) and syringaldehyde (14) (see Tables 4.3a and b). Again a phenolic hydroxyl group was present in all these species except for benzoquinone.

##### *Quinonoid species*

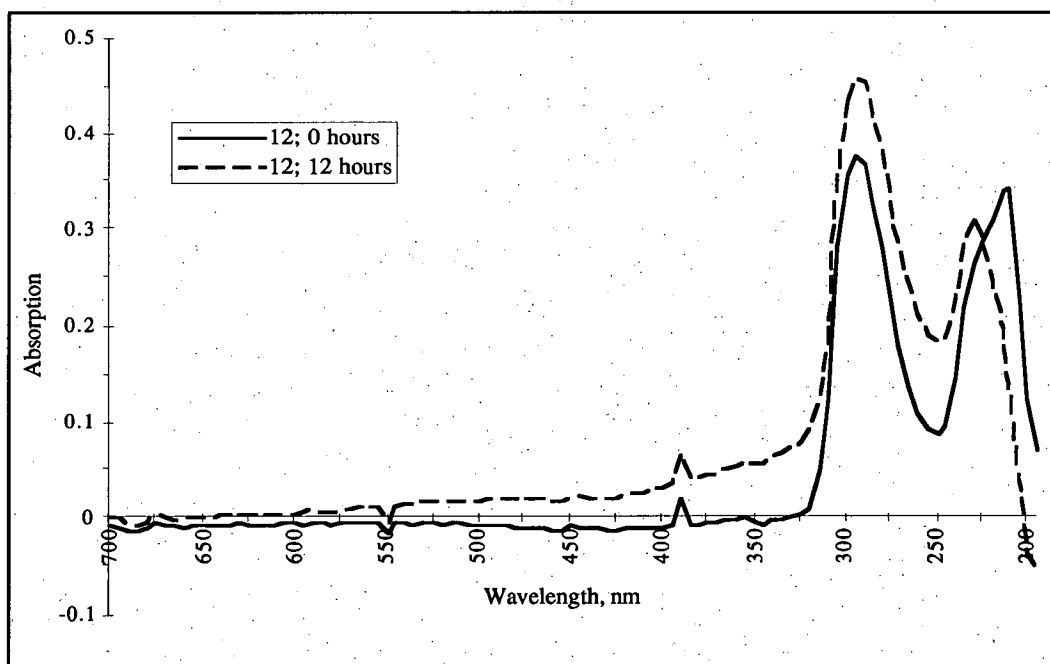
While benzoquinone experienced a diminished redness (decrease in  $a^*$ ) the other quinone species exhibited an increase in redness or  $a^*$  (see Table 4.3b). The UV-visible absorption spectra for these compounds before and after irradiation are shown in Figures 4.16, 4.17 and 4.18.



**Figure 4.16.** UV-visible absorption spectra for 1,4-benzoquinone before and after 12 hours of irradiation by Ultravitalux sunlamps.



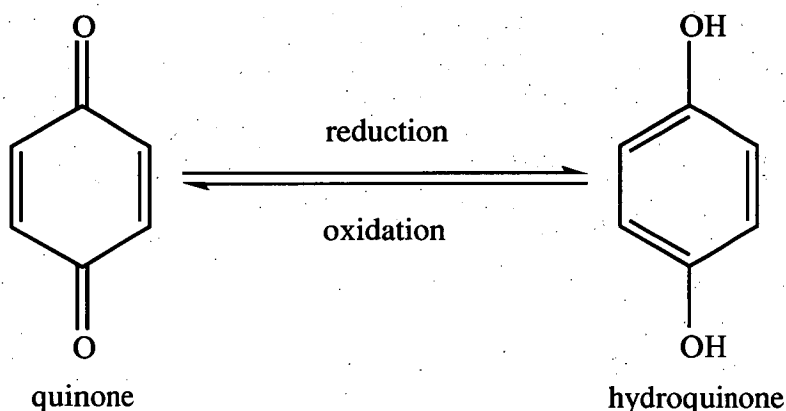
**Figure 4.17.** UV-visible absorption spectra for methoxyhydroquinone before and after 12 hours of irradiation by Ultravitalux sunlamps.



**Figure 4.18.** UV-visible absorption spectra for methylhydroquinone before and after 12 hours of irradiation by Ultravitalux sunlamps.

### Initial observations

The absorption spectra for both non-irradiated methoxyhydroquinone (Figure 4.17) and methylhydroquinone (Figure 4.18) compounds revealed large absorption peaks at 290-295nm, which is characteristic of the hydroquinone group<sup>74</sup>. The absorption spectra for non-irradiated 1,4-benzoquinone (Figure 4.16) also revealed a peak in this region, although it was less intense (relative to its other absorption peaks) than for the previous two compounds. This suggests that the 1,4-benzoquinone sample may have contained some hydroquinone contaminant. It is well known that quinone and hydroquinone are readily interconverted by the redox (reduction-oxidation) equilibrium shown below:



It is therefore possible that the 1,4-benzoquinone sample had formed some hydroquinone compound, and established the redox equilibrium shown above, prior to irradiation. The need for a phenolic hydroxyl group for reversion to occur has previously been shown (see Category 1 compounds). The establishment of the above redox system in the 1,4-benzoquinone sample may explain the photo-induced reversion observed by this sample, as although benzoquinone contains no phenolic hydroxyl groups, its redox partner (hydroquinone) contains two.

Looking again at the absorption spectra for the non-irradiated quinonoid compounds (Figures 4.16-4.18), both spectra for 1,4-benzoquinone and methoxyhydroquinone contain broad absorption peaks at 350nm (tailing to about 430nm), but the methylhydroquinone spectra does not. This is characteristic of the quinone group<sup>74</sup>. The presence of this absorption in the methoxyhydroquinone sample suggests that it had also established a redox system prior to irradiation, similar to that for 1,4-benzoquinone shown above. Therefore the sample would have contained both methoxyhydroquinone and its redox partner, methoxyquinone. Castellan et al.<sup>112</sup> found that methoxyquinone formed when they dissolved methoxyhydroquinone in the solvent THF. They attributed this to the formation of peroxidic radicals by the solvent, which could then easily oxidise methoxyhydroquinone. This was not likely

to be the case in the present study, as DMF does not form peroxidic radicals, nor is it prone to oxidise substrates. Furthermore, preliminary tests on DMF revealed that this solvent had no significant effect on methoxyhydroquinone (see Section 4.2.2). It is therefore likely that the oxidation of methoxyhydroquinone occurred under atmospheric conditions prior to measurements being taken.

The absence of any absorption above 320nm for the methylhydroquinone spectra suggests that this sample had not established a redox pair before irradiation.

### *The effects of irradiation*

**Methylhydroquinone.** Upon irradiation, methylhydroquinone exhibited a typical reversion response in its UV-visible absorption spectrum (Figure 4.18), with the introduction of absorption above 320nm, including a broad peak at 350nm, indicating the formation of coloured quinone species. A disappearance of an absorption peak at 210nm, and hyperchromic effects in a shoulder at 230nm and a peak at 290-295nm were also apparent. A small broad peak introduced around 525nm upon irradiation could indicate dimerisation and cyclisation products<sup>112</sup>. This was confirmed in the mass spectra, (see Appendix A), which revealed the presence of dimers with MW of 246. It is possible that these dimers could have been oligomers, formed via a similar mechanism to that discussed for guaiacol (see compounds of Category 2). Studies by Forsskåhl et al.<sup>72</sup> on the effect of irradiation on methoxyhydroquinone systems have shown that these compounds first oxidised to benzoquinones, then dimerised to form hydroquinone-quinone and bisquinone dimers, which then cyclised to form hydroxy-dibenzofuran-quinones (this is shown in more detail below in Figure 4.19, where methoxyhydroquinone is discussed). If methylhydroquinone had undergone similar dimerisation and cyclisation processes, then its analogous reaction intermediates and products would have been methyl-*p*-quinone (M.W. 122), 5-methyl-2-(2,5-dihydroxy-4-methylphenyl)-1,4-benzoquinone (M.W. 244), 4,4'-dimethylbiphenyl-2,5,2',5'-bisquinone (M.W. 242), and 8-hydroxy-3,7-dimethyldibenzofuran-1,4-quinone (M.W. 242). The mass spectra for irradiated methylhydroquinone did reveal small amounts of species with each of the above molecular weights, so it is possible that methylhydroquinone had dimerised and cyclised in this manner.

The presence of a fragment of lower molecular weight (M.W. 107) in the mass spectra for irradiated methylhydroquinone could also indicate demethylation of a quinone product or dimerisation intermediate (i.e. equivalent to methylhydroquinone minus two hydrogen atoms and one methyl group), resulting in an unsubstituted quinone species.

**1,4-Benzoquinone.** 1,4-benzoquinone revealed significant reversion changes in its UV-visible absorption spectra (Figure 4.16) upon irradiation, similar to those already discussed for methylhydroquinone. The main difference is that the broad absorption above 320nm was already present for non-irradiated 1,4-benzoquinone, and so had not been introduced by irradiation but increased.

The absorption peaks at 320nm (attributed to the hydroquinone redox partner) and 350nm (attributed to the quinone species) had both increased in intensity, relative to other peaks in the spectrum. Several studies have shown that methoxy-*p*-benzoquinone species undergo a rapid initial photo-reduction stage to form their methoxy-*p*-hydroquinone counterpart, followed by a slower photo-oxidation stage to reform the original benzoquinone species<sup>71,112</sup>. It is possible that a similar photo-reduction - photo-oxidation cycle had occurred for 1,4-benzoquinone, resulting in an increase in absorption at the respective spectral regions for benzoquinone and hydroquinone.

In addition to this, the hydroquinone redox partner present in the sample prior to irradiation may also have undergone photo-oxidation reactions.

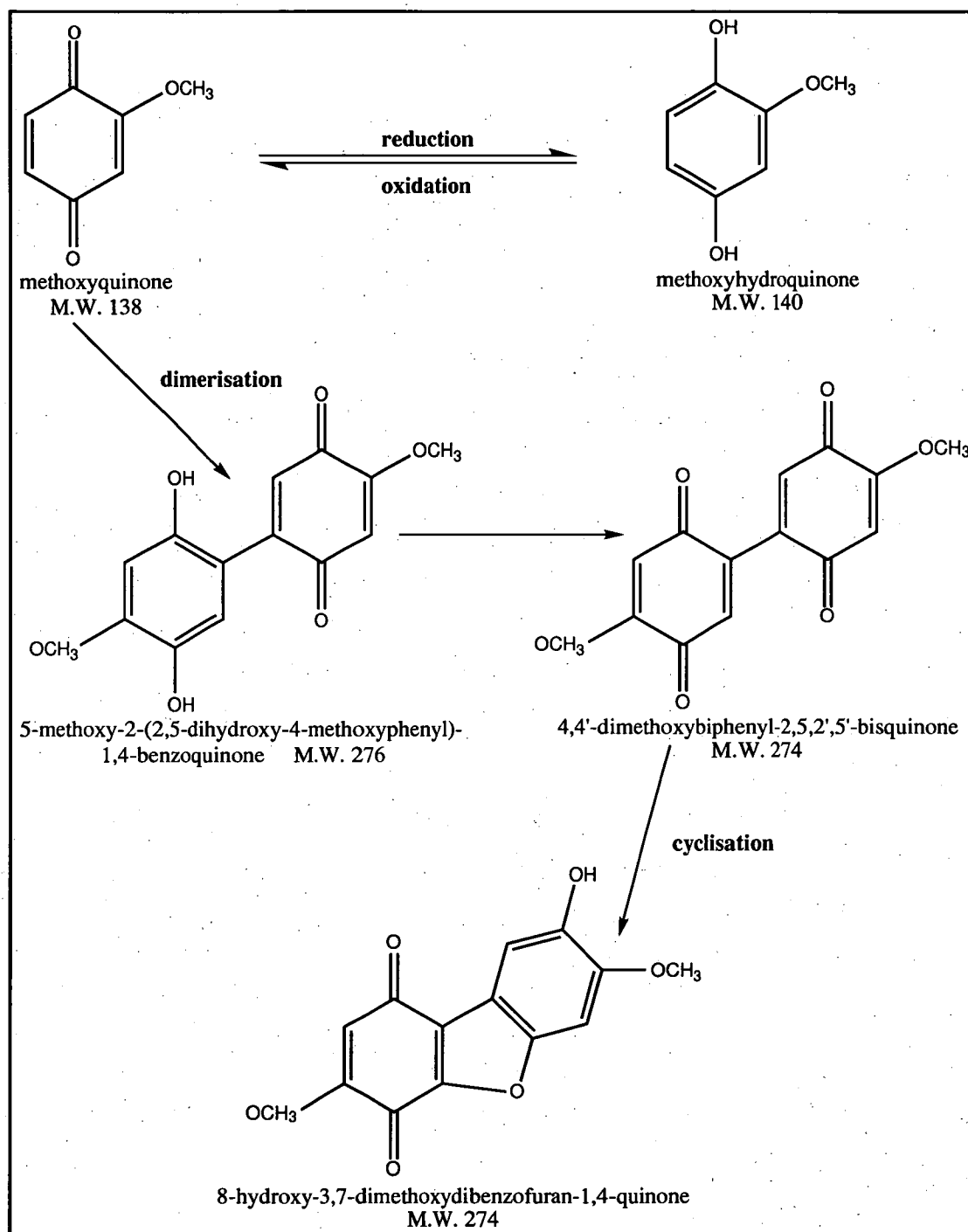
A small increase in absorption around 525nm was also apparent on the UV-visible absorption spectra for 1,4-benzoquinone upon irradiation, which could be due to the formation of dimers or cyclisation products as well as those processes already mentioned. Oligomerisation involving H-abstraction at the phenolic hydroxyl group as described for guaiacol above, is also an option for this compound's redox partner.

Thus the photo-induced reversion of this sample is quite complicated, due to simultaneous processes occurring which involve different components of the sample.

**Methoxyhydroquinone.** No significant changes were observed in the absorption spectra upon irradiation of methoxyhydroquinone (see Figure 4.17), despite changes having been observed in the colour parameters (see Tables 4.2 and 4.3). This is possibly due to a series of simultaneous reactions occurring (as for 1,4-benzoquinone discussed above), involving different components of the redox system pre-established in the sample, whose effects on the absorption spectrum mutually cancel each other.

The mass spectra for methoxyhydroquinone, (see Appendix A), revealed that dimers had again formed (with M.W. of 278). It is possible that this occurred via the same oligomerisation mechanism as discussed for guaiacol (see compounds of Category 2). Alternatively the MLC may have undergone oxidation, dimerisation and cyclisation processes, resulting in the formation of the red-coloured dibenzofuran-

1,4-quinone species, as was shown to occur for these species upon irradiation by Forsskåhl et al.<sup>72</sup>. This scheme has been reproduced in Figure 4.19.



**Figure 4.19.** Photo-induced oxidation/reduction, dimerisation and cyclisation processes for methoxyhydroquinone and methoxyquinone systems<sup>72</sup>.

The mass spectra for irradiated methoxyhydroquinone (see Appendix A) did reveal species with molecular weights corresponding to those of each species presented in Figure 4.19 (albeit to small degrees), so the reaction scheme shown in this figure is certainly plausible. The dimers and cyclisation products shown in Figure 4.19

should have resulted in an increase in absorption between 500 and 550nm in the UV-visible absorption spectra. The UV-visible absorption spectra (Figure 4.17), however, did not reveal any increase in absorption in this region upon irradiation. Furthermore, absorption in this region was present prior to irradiation. It is possible that these processes may have been initiated by atmospheric oxidation prior to irradiation. Indeed, the mass spectra before irradiation, (see Appendix A), did reveal the presence of a dimer with molecular weight of 278. The quinone species (M.W. 138) was also present prior to irradiation, as was suspected due to the establishment of the redox equilibrium discussed previously. Species with molecular weights of 276 and 274 may have been present in very small amounts, but the height of their signals was close to that of the noise interference of the spectra, so their presence is not conclusive. Nevertheless, the signals for each of the molecular weights corresponding to each of these products were more intense in the mass spectra for the irradiated sample than for the non-irradiated sample. Therefore, it is possible that each of the reactions discussed above may have been initiated by atmospheric oxidation, and then enhanced by irradiation.

The mass spectra for irradiated methoxyhydroquinone also detected a lower molecular weight fragment corresponding to a demethylation process (M.W. 125). This was also present in the non-irradiated sample, however, so could represent an atmospheric oxidation process.

#### *Summary for quinonoid species*

Each quinonoid species may have undergone similar photo-reactions, but to differing degrees, dependent on the form of the quinone species and the position of equilibrium of redox partners present in the sample. These reactions included dimerisation and cyclisation, and possibly demethylation processes.

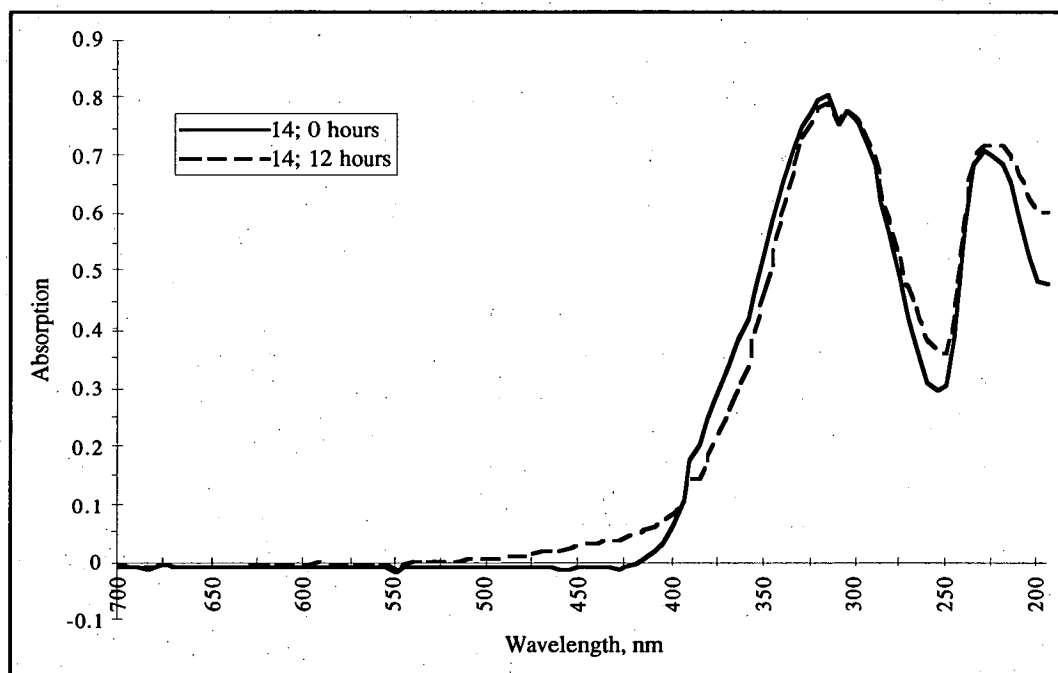
The photo-reactions of methoxyhydroquinone, (and possibly also 1,4-benzoquinone), appeared to be similar to atmospheric oxidation reactions, except that they were further enhanced by irradiation.

Atmospheric oxidation of methoxyhydroquinone and 1,4-benzoquinone had also resulted in the establishment of a quinone-hydroquinone redox system prior to irradiation. Methylhydroquinone did not undergo atmospheric oxidation prior to irradiation, and a redox hydroquinone-quinone system was not established in the sample.



## Syringaldehyde

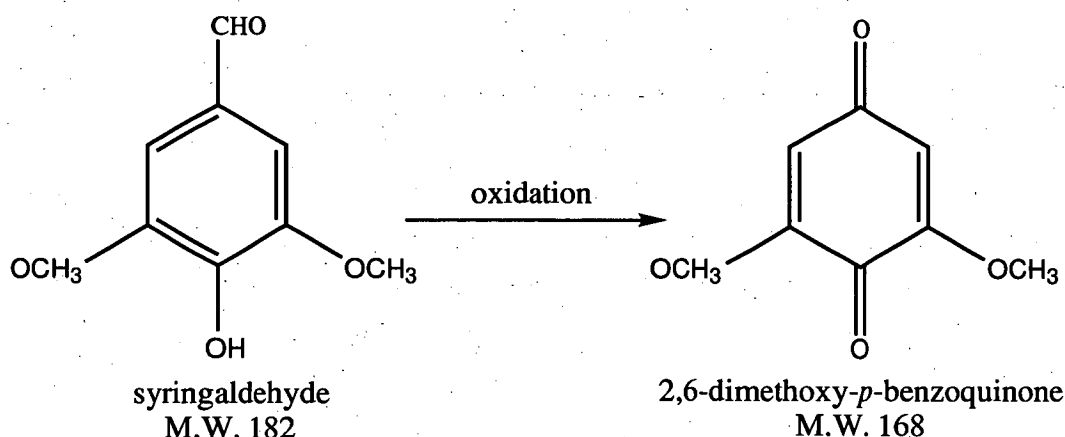
Tables 4.3a and b revealed that upon irradiation syringaldehyde acquired a faint green colour (decrease in  $a^*$ , with negative values), along with the other common changes in colour parameters indicative of reversion (increases in  $k$  and  $b^*$  and a decrease in  $L^*$ ). Like the majority of the compounds discussed so far which had experienced yellowing, it also contained a phenolic hydroxyl group, along with methoxyl groups and a C=O group. Its UV-visible absorption spectra, (shown in Figure 4.20), revealed only small changes due to irradiation, but these were in areas similar to those already discussed for compounds that had undergone reversion or discolouration. These included a small increase in absorption at 220nm, and the introduction of a broad “yellowing” peak at about 440nm. This latter peak was also observed in the spectra for irradiated vanillin (see Figure 4.15), and can be attributed to the formation of quinone species.



**Figure 4.20.** UV-visible absorption spectra for syringaldehyde before and after 12 hours of irradiation by Ultravitalux sunlamps.

As found for vanillin (see Category 2 compounds), the mass spectra for irradiated syringaldehyde (see Appendix A) revealed the presence of an ion fragment corresponding to the MLC minus one hydrogen atom (M.W. 181), which is characteristic of aldehydes. A lower molecular weight fragment corresponding to the MLC minus a  $\text{CH}_3$  group (M.W. 167) was also detected. It was suggested for vanillin that this latter peak could have resulted from a demethylation process, or it could have been due to the formation of the corresponding benzoquinone species,

which in the case of syringaldehyde is 2,6-dimethoxy-*p*-benzoquinone (M.W. 168). Syringaldehyde was also shown by Dimmel et al.<sup>116</sup> to form its corresponding quinone species on oxidation by NO<sub>2</sub>. As with vanillin, Dimmel et al. proposed that the first step in this process was a hydrogen abstraction from the phenolic hydroxyl group. Syringaldehyde and its corresponding quinone species, 2,6-dimethoxy-*p*-benzoquinone, are shown below:



This product could be responsible for the absorption at 440nm seen in the absorption spectra for the irradiated sample.

Therefore syringaldehyde may have undergone hydrogen abstraction, cleavage of methyl groups, and/or production of its corresponding benzoquinone species upon irradiation. Once again these conclusions are tentative, as each of the fragments discussed may alternatively have been products of ionisation processes during mass spectrometry. Absorption at 440nm in the UV-visible absorption spectra for irradiated syringaldehyde, however, provided supporting evidence for the formation of benzoquinone species.

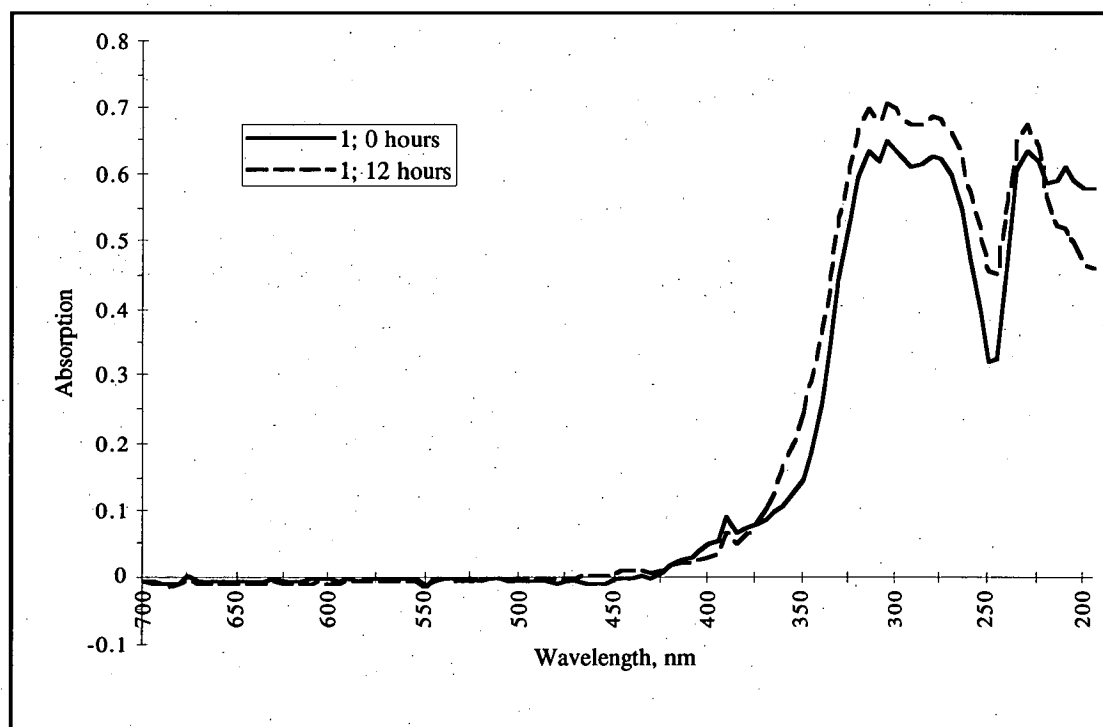
Unlike most MLCs discussed so far which underwent photo-discolouration, the mass spectra for irradiated syringaldehyde did not reveal the presence of dimeric structures. Oligomerisation as discussed for guaiacol above could not have occurred for syringaldehyde, as it requires free positions on the benzene ring either *ortho* or *para* to the phenolic hydroxyl group. Syringaldehyde is substituted at each of these positions.

#### 4.3.5 Category 4 compound: Yellowing with no associated darkening

Tables 4.3a and b showed that irradiation of acetovanillone had resulted in an increase in chromophore content (increase in *k*), with associated yellowing (increase in *b*\*) and decreasing redness (decrease in *a*\*), but no darkening (constant *L*\*). It is noteworthy that once again C=O, phenoxy hydroxyl and methoxyl groups were

present. Like many of the MLCs already discussed, the UV-visible absorption spectra revealed a significant decrease in absorption at 210nm (see Figure 4.21). All other peaks experienced a hyperchromic effect, except for a peak at 390nm which underwent no significant change after irradiation. A small shouldering peak was introduced at around 360nm, which is indicative of the formation of coloured quinone species. So while no darkening was observed, the irradiation responses still appeared typical with respect to those already discussed.

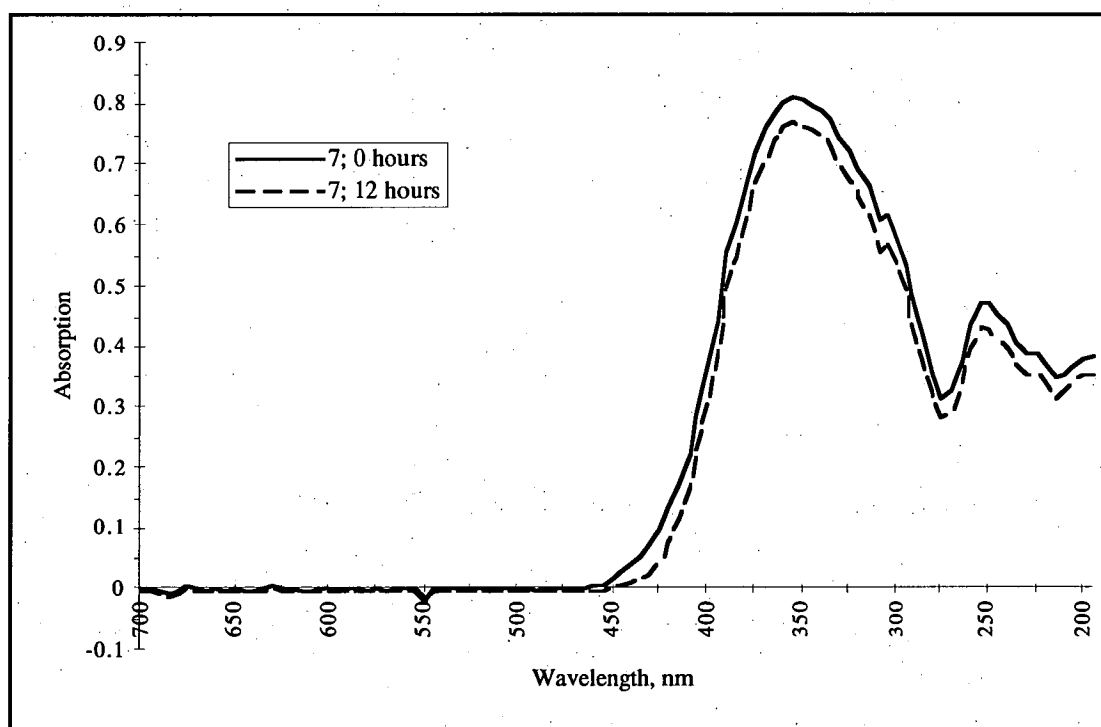
The mass spectra of the irradiated sample (see Appendix A) again revealed the presence of dimers (of MW 330), which could have been formed via H-abstraction and oligomerisation steps as previously shown for guaiacol (see Category 2 compounds). Fragments were also detected which may indicate several different reversion products. These include fragments of molecular weight corresponding to a loss of a  $\text{CH}_3$  group (MW 151), a loss of a  $\text{CH}_3$  group and a hydrogen atom which could be the corresponding quinone species (MW 150), and a fragment with molecular weight of 123 which could represent the loss of the  $\text{CH}_3\text{C}=\text{O}$  end group, possibly via a Norrish-type 1 cleavage of the carboxyl-carbon to ring-carbon bond.



**Figure 4.21.** UV-visible absorption spectra for acetovanillone before and after 12 hours of irradiation by Ultravitalux sunlamps.

#### 4.3.6 Category 5 compound: Small darkening but no photo-yellowing

Although no chromophore production was observed (constant  $k$ ), and yellowing did not increase (in fact a small decrease in  $b^*$  was found, indicating a possible minor photo-bleaching effect), a small darkening (decrease in  $L^*$ ) and diminished green colour (decrease in  $a^*$ , with negative values) was observed for 4-hydroxy-3-methoxy cinnamaldehyde (see Tables 4.3a and b). This indicated that a photo-reaction may have occurred which was distinct from the reversion responses already discussed. The UV-visible absorption spectra (Figure 4.22), however, revealed no significant changes, except possibly a very small hypochromic effect across the whole spectrum, and a removal of absorption between 430 and 440nm. This would certainly indicate a small bleaching effect, or removal of coloured species.



**Figure 4.22.** UV-visible absorption spectra for 4-hydroxy-3-methoxy cinnamaldehyde before and after 12 hours of irradiation by Ultravitalux sunlamps.

Chapter 2 introduced coniferaldehyde species (such as this compound) as being a difference between TMP and peroxide bleached TMP (BTMP), since peroxide bleaching removes these species (Reaction 1, Section 2.3.3). It was also suggested in Chapter 2 that coniferaldehydes undergo photo-induced cleavage in TMP, to form vanillin structures and conjugated ketones (Reaction 2, Section 2.3.3). This was supported by the UV-visible absorption difference spectra for irradiated TMP against non-irradiated TMP (Figure 2.5b, Section 2.3.3), with a decrease in absorption at

360nm indicating a removal of coniferaldehyde species, and an increase in absorption at 330nm representing a production of conjugated ketone species. This reaction does not appear to be the case for this compound on its own, however, as its absorption spectrum (Figure 4.22) did not undergo similar changes to those previously shown for TMP on irradiation. Although these results suggest that the proposed reaction introduced in Chapter 2 is wrong, it cannot be disregarded, as influences of surrounding lignin components, along with steric effects, could alter the reactions seen for coniferaldehydes alone in solution and coniferaldehydes incorporated within a complex solid lignin matrix.

On a further note, BTMP was found to undergo a greater extent of reversion than TMP in Chapters 2 and 3. This was attributed to a reformation of coniferaldehyde species during irradiation of BTMP handsheets. The reaction scheme proposed for the initial bleaching (or removal) of these species by peroxide was shown in Chapter 2, Reaction 1. One of the products of this reaction is vanillin. While the coniferaldehyde species in this section did not undergo reversion, vanillin was shown (as a Category 1 compound), to have photo-yellowed. Therefore the introduction of vanillin into BTMP handsheets could further explain their greater extent of reversion.

Like the previous compounds discussed, which underwent significant photo-yellowing, 4-hydroxy-3-methoxy cinnamaldehyde also contained phenolic hydroxyl and methoxyl groups and a C=C bond, but in addition had an aldehyde end group on the 3-carbon side chain. Interestingly, this is structurally similar to ferulic acid (discussed in Category 1), which also did not photo-yellow, except that ferulic acid had a COOH end group. It is possible that the presence of a COOH or CHO end group in conjugation with a photo-sensitiser group on a 3-carbon side chain interferes with photo-yellowing processes. This is supported by comparing the responses of these two compounds with isoeugenol, which did yellow. Isoeugenol is structurally identical to both ferulic acid and 4-hydroxy-3-methoxy cinnamaldehyde, except it has a methyl end group. Therefore, it is possible that the COOH or CHO end group may have deactivated the sensitisation of its conjugated neighbouring C=C group, or interfered with the H-abstraction step and/or the final oxidation. If the latter possibilities were the case, then it would follow that compounds containing only COOH, phenoxy hydroxyl and methoxyl groups, (i.e. contain no second (conjugated) sensitiser group), would also not yellow. Vanillic acid contained these three groups only, but did photo-yellow. Thus, in vanillic acid, the COOH group had not hindered the yellowing process. Therefore, it is likely that side chain COOH and CHO end groups deactivate the initial excitation of conjugated sensitiser groups.

#### 4.4 Conclusions

- Except for 1,4- benzoquinone, all MLC compounds lacking a phenolic hydroxyl group did not photo-yellow. Many of these compounds, however, could still play an indirect role in lignin photo-yellowing by behaving as photo-sensitisers to yellowing reactions (for example benzophenone).
- Each MLC that underwent photo-induced discolouration contained a phenolic hydroxyl group, confirming its involvement as a photo-reactive centre. 1,4-benzoquinone was the exception, but this still may have contained a phenolic hydroxyl group, as an equilibrium redox system was established in the sample prior to irradiation. Thus the 1,4-benzoquinone sample contained two phenolic hydroxyl groups on its redox partner, 1,4-hydroquinone.
- The presence of a side chain C=O or C=C group (e.g. acetovanillone, eugenol), or a ring-substituted COOH or CHO group (e.g. vanillic acid, vanillin), in conjunction with a phenolic hydroxyl group, may have enhanced photo-reversion by acting as photo-sensitising groups.
- Compounds which contained a COOH or CHO end group in conjugation with a 3-carbon side chain C=C photo-sensitising group (e.g. ferulic acid, 4-hydroxy-3-methoxy cinnamaldehyde) did not photo-revert. These end groups appeared to interfere with the sensitisation step.
- Quinone and hydroquinone compounds photo-yellowed efficiently, irrespective of methyl or methoxyl substituents. The unsubstituted quinone and methoxyl-substituted hydroquinone samples established a redox system, and developed some oxidation products under atmospheric conditions prior to irradiation. The methyl-substituted hydroquinone did not form any oxidation products, nor did it establish a redox system prior to irradiation.
- Most compounds underwent oligomerisation upon irradiation, which was likely to have occurred via H-abstraction, with subsequent formation of radicals which could then have combined (e.g. guaiacol). Alternate mechanisms are also possible, however.
- Although many compounds were found to have possibly formed quinone species, few compounds showed conclusive evidence for this.

Many compounds may have also formed quinonoid radicals as possible intermediates.

- Cleavage of simple substituted groups (i.e. demethylation and/or demethoxylation) was also found to be a possibility for many irradiated compounds, perhaps also resulting in the formation of radicals. This was also not conclusive, however.
- Several different reversion pathways may have occurred for one type of MLC, such as oxidation, oligomerisation/dimerisation, bond cleavage (for example demethylation and/or demethoxylation), and formation of quinonoid species.
- Hydrogen abstraction steps may be involved in many of the reversion processes, particularly about the phenolic hydroxyl groups.

The compounds which were shown to undergo photo-yellowing were used for further studies on the abilities of mercaptans to inhibit this process. These studies are discussed in Chapter 5.

## **CHAPTER 5**

# **INHIBITION OF REVERSION BY MERCAPTANS - MODEL LIGNIN COMPOUND STUDIES**

### **5.1 Introduction**

The three mercaptans introduced in Chapter 3 were applied to several MLCs and then irradiated in order to determine what kinds of MLCs the mercaptans are active towards in inhibiting photo-induced discolouration. The MLCs selected for these studies were determined from the results presented in Chapter 4. As discussed in Chapter 4, five distinct reversion effects were apparent for a range of MLCs, based on changes in their tristimulus colour parameters  $L^*$ ,  $a^*$  and  $b^*$ , and absorption coefficients,  $k$ . These were categorised into five groups, and this categorisation will be continued in this chapter for simplicity. One of these categories contained MLCs which did not undergo any photo-induced changes in the colour parameters or absorption coefficients, and so will not be discussed further. The remaining categories (2-5) were treated with the mercaptans and irradiated to gauge inhibition of their photo-reactions in this chapter.

### **5.2 Experimental Procedures**

The MLCs were irradiated in an identical manner and for an identical length of time (12 hours) as in Chapter 4. All samples were irradiated as  $0.5 \pm 0.1\%$  MLC solutions in DMF and mercaptans were also added at concentrations of  $0.5 \pm 0.1\%$ . Sampling and taking of measurements was performed as previously described in Chapter 4.

### **5.3 Results and Discussion**

#### **5.3.1 Mercaptan controls**

Table 5.1 shows the absorption coefficients,  $k$ , and the tristimulus colour parameters,  $L^*$ ,  $a^*$  and  $b^*$ , for mercaptan controls, (i.e.  $0.5 \pm 0.1\%$  mercaptan in DMF solutions), before and after irradiation by the Ultravitalux lamps for 12 hours.



**Table 5.1.** The absorption coefficients,  $k$  ( $\text{g/m}^2$ )<sup>-1</sup>, and tristimulus colour parameters,  $L^*$ ,  $a^*$  and  $b^*$ , for mercaptan controls before and after 12 hours of irradiation by Ultravitalux sunlamps.

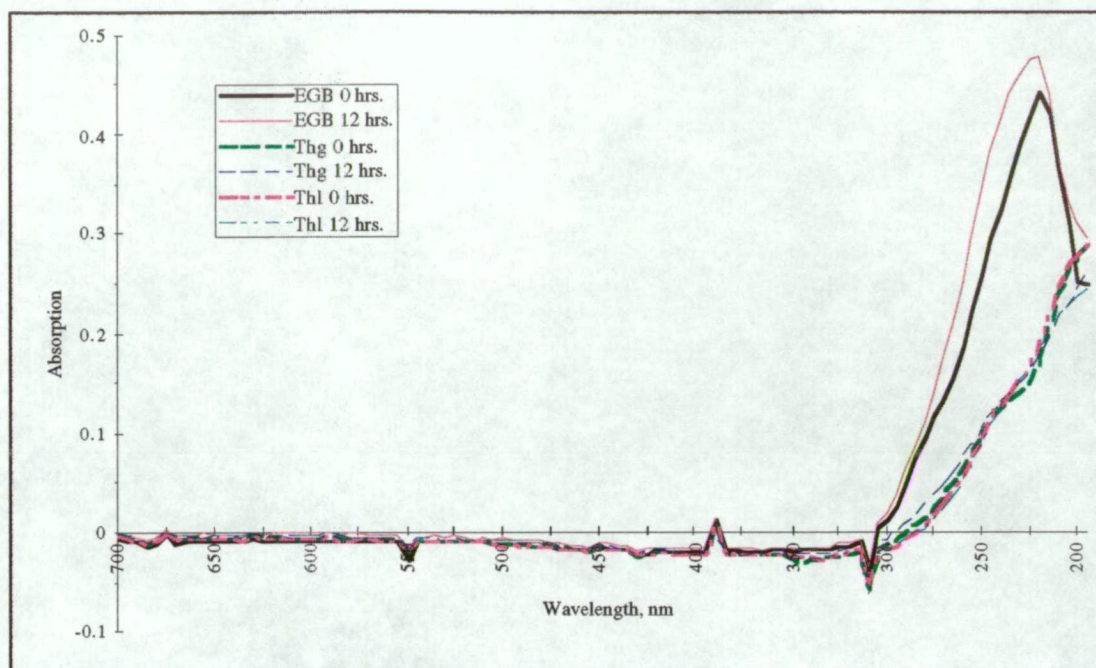
Mercaptan	k 0 hours	k 12 hours	$\Delta k_{12-0 \text{ hours}}$
EGB	1.0	0.9	-0.1
Thg	1.4	1.5	0.1
Thl	1.4	1.4	0.0
	$b^*$ 0 hours	$b^*$ 12 hours	$\Delta b^*_{12-0 \text{ hours}}$
EGB	0.8	0.7	-0.1
Thg	1.5	1.8	0.3
Thl	1.5	1.7	0.2
	$L^*$ 0 hours	$L^*$ 12 hours	$\Delta L^*_{12-0 \text{ hours}}$
EGB	98.03	98.18	$0.15 \pm 0.03$
Thg	98.26	98.24	$-0.02 \pm 0.03$
Thl	98.27	98.25	$-0.02 \pm 0.03$
	$a^*$ 0 hours	$a^*$ 12 hours	$\Delta a^*_{12-0 \text{ hours}}$
EGB	0.1	0.1	0.0
Thg	-0.2	-0.2	0.0
Thl	-0.2	-0.2	0.0

Note that standard deviations are  $\pm 0.1$  for  $k$ ,  $b^*$  and  $a^*$  and  $\pm 0.02$  for  $L^*$  unless otherwise stated.

All controls appeared colourless both before and after irradiation.

From the colour parameters in Table 5.1 it can be seen that EGB has imparted no change to the previously established colourless DMF solvent (see Chapter 4, Section 4.3.1), but Thg and Thl may have introduced a very small yellowing (i.e. small increase in  $b^*$ ). This is likely to be due to a small colouration of the mercaptans themselves, which was not discernible by eye. For the following discussions any changes below these values will be assumed to be due to this inherent colouration of the two mercaptans, and therefore discounted as possible interactions between mercaptans and MLCs.

It is also apparent from Table 5.1 that no significant reversion had occurred for any of the mercaptan controls, as the absorption coefficients and colour parameters did not change significantly after irradiation. The UV-visible absorption spectra for the three mercaptans before and after irradiation are shown in Figure 5.1.

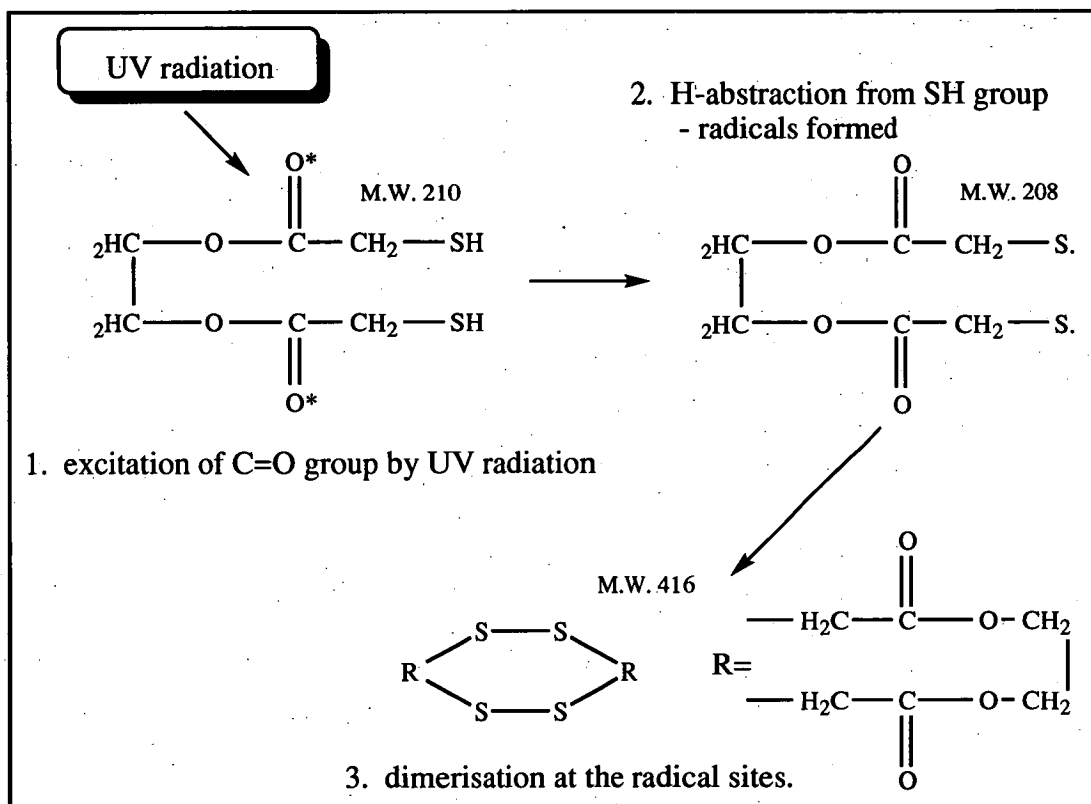


**Figure 5.1.** UV-visible absorption spectra for mercaptans in DMF solutions before and after 12 hours of irradiation by Ultravitalux sunlamps.

The peaks for all the mercaptans are distinctive and will be taken into account for the following MLC-mercaptan interpretations. A small hyperchromic effect at 195nm for each mercaptan after irradiation could have resulted from photo-activity about the carbonyl groups in EGB, and carboxyl groups in Thg and Thl. As this wavelength is at the edge of the spectrophotometer's range, however, it is subject to larger error fluctuations, and therefore is not a reliable indication of spectral activity. Furthermore, it is also within the range of maximum absorption found for the solvent, DMF, shown in Chapter 4, Figure 4.4, (along with a large absorption at 220nm observed in each spectra).

No other significant changes between the non-irradiated and irradiated spectra were observed for Thg and Thl, so it is possible that no photo-reactive changes had occurred. EGB, on the other hand, exhibited a small hyperchromic effect between 220nm and 270nm after irradiation. This could have resulted from photo-activity about its C=O groups, which absorb at 195nm and between 270 and 285nm. Alternatively, the increases in these peaks could have been due to the formation of disulphide bonds, which also absorb in this region (195nm and 255nm). The mass spectra of irradiated EGB (see Appendix B) confirms the latter as a possibility, as the presence of EGB dimers minus 4 hydrogen atoms (MW 416) was revealed. It should be noted that the mass spectra for the non-irradiated EGB sample (see Appendix B) also revealed the presence of this dimer, but to a lesser extent. It is therefore possible that the dimerisation of EGB was initiated by atmospheric oxidation, and then enhanced by irradiation.

It is common for compounds containing thiol end groups to undergo photo-induced H-abstraction of the hydrogen directly attached to the sulphur atom<sup>115</sup>. It is therefore possible that each of the C=O groups had become sensitised by the UV radiation and then initiated abstraction of hydrogen from the SH end groups to create RS· radicals. These radicals could then have combined to form a dimer across disulfide bonds. This is shown in the reaction scheme below (Reaction 3).



**Reaction 3.** Possible photo-induced dimerisation of EGB across disulphide bonds.

It is also possible that the MW 208 structure could simply have undergone intra-molecular ring closure to form a ten-membered ring containing one disulphide bond. It should be kept in mind that other peaks were also present, some with large molecular weights and others being fragments, so that other reactions could also have occurred.

Interestingly, despite the lack of changes in both the colour parameters and the UV-visible absorption spectra for irradiated Thg and Thl, their mass spectra also revealed the presence of dimers minus 2 hydrogen atoms per sulphur atom (MW 182 for Thg, and 210 for Thl), among other peaks. It is possible, therefore, that Thg and Thl also underwent a similar reaction to the dimerisation discussed for EGB.

### 5.3.2 Category 2 compounds: Reversion with no change in the red-green colour coordinate a\*

The observations of colour changes upon treatment with mercaptans and subsequent irradiation for 12 hours by Ultravitalux sunlamps of MLCs, which were previously established as Category 2 compounds in Chapter 4, are shown in Table 5.2. Changes in the absorption coefficients,  $k$ , and the tristimulus colour parameters  $L^*$ ,  $a^*$  and  $b^*$  are shown in Tables 5.3a-d. Included in each table are the results of irradiation of the untreated MLC samples, reviewed from Chapter 4, to simplify comparisons.

The postscripts in Tables 5.3 refer to: a. Reversion of the untreated MLC (reviewed from Chapter 4); b. Bleaching by mercaptans (indicated by decreases in  $k$  (Table 5.3a),  $b^*$  (5.3b), and  $a^*$  (5.3d), and an increase in  $L^*$  (5.3c)); and c. Reversion of the mercaptan-treated MLC, (indicated by increases in  $k$  (Table 5.3a),  $b^*$  (5.3b), and  $a^*$  (5.3d), and a decrease in  $L^*$  (5.3c)). The standard deviations are  $\pm 0.1$  for Tables 5.3a, b & d, and  $\pm 0.02$  for Table 5.3c, unless stated otherwise.

**Table 5.2.** Observations of the colour of MLC solutions treated with mercaptans and irradiated for 12 hours by Ultravitalux sunlamps.

MLC	original	<sup>a</sup> irradiated	mercaptan	treated	treated and irradiated
eugenol	colourless	pale yellow	EGB	colourless	yellow tinge
			Thg	colourless	pale yellow
			Thl	colourless	yellow
guaiacol	colourless	pale orange	EGB	colourless	colourless
			Thg	colourless	colourless
			Thl	colourless	yellow tinge
isoeugenol	colourless	orange tinge	EGB	colourless	colourless
			Thg	colourless	colourless
			Thl	colourless	colourless
vanillic acid	colourless	light orange-yellow	EGB	colourless	colourless
			Thg	colourless	pale yellow
			Thl	colourless	yellow tinge
vanillin	colourless	light orange	EGB	colourless	dark yellow
			Thg	colourless	orange
			Thl	colourless	orange

<sup>a</sup>Reversion of the untreated MLCs, reviewed from Chapter 4.

**Table 5.3a.** Changes in the absorption coefficients,  $k$  ( $\text{g/m}^2$ )<sup>-1</sup>, for MLCs treated with mercaptans and irradiated for 12 hours by Ultravitalux sunlamps.

MLC	<sup>a</sup> reversion: $\Delta k_{(12\text{hrs}-0\text{hrs})}$	mercaptan	<sup>b</sup> bleaching: $\Delta k_{(\text{treated}-\text{untreated})}$	<sup>c</sup> reversion: $\Delta k_{(12\text{hrs}-0\text{hrs})}$
eugenol	0.6	EGB	0.1	0.5
		Thg	0.0	0.5
		Thl	0.0	0.6
guaiacol	0.8	EGB	0.0	-0.1
		Thg	-0.1	0.0
		Thl	-0.1	0.1
isoeugenol	0.5	EGB	0.0	0.1
		Thg	-0.2	-0.2
		Thl	-0.3	0.0
vanillic acid	1.0	EGB	0.2	-0.2
		Thg	0.1	0.0
		Thl	0.1	0.1
vanillin	5.2±0.4	EGB	-1.9	2.6
		Thg	-2.1	2.5
		Thl	-2.1	2.6

**Table 5.3b.** Changes in  $b^*$  for MLCs treated with mercaptans and irradiated for 12 hours by Ultravitalux sunlamps.

MLC	<sup>a</sup> reversion: $\Delta b^*_{(12\text{hrs}-0\text{hrs})}$	mercaptan	<sup>b</sup> bleaching: $\Delta b^*_{(\text{treated}-\text{untreated})}$	<sup>c</sup> reversion: $\Delta b^*_{(12\text{hrs}-0\text{hrs})}$
eugenol	0.6	EGB	-0.2	0.7
		Thg	0.2	0.5
		Thl	-0.4	1.3
guaiacol	0.9	EGB	-0.2	0.0
		Thg	-0.1	0.1
		Thl	-0.3	0.4
isoeugenol	0.6	EGB	-0.4	-0.6
		Thg	-0.2	-0.5
		Thl	-0.8	0.2
vanillic acid	1.3	EGB	-0.1	-0.1
		Thg	-0.1	0.3
		Thl	-0.3	0.5
vanillin	3.2±0.4	EGB	-2.4	3.0
		Thg	-2.3	3.1
		Thl	-2.6	3.2

**Table 5.3c.** Changes in L\* for MLCs treated with mercaptans and irradiated for 12 hours by Ultravitalux sunlamps.

MLC	<sup>a</sup> reversion: $\Delta L^*$ (12hrs-0hrs)	mercaptan	<sup>b</sup> bleaching: $\Delta L^*$ (treated-untreated)	<sup>c</sup> reversion: $\Delta L^*$ (12hrs-0hrs)
eugenol	-0.26	EGB	-0.12±0.04	-0.33±0.04
		Thg	0.11±0.04	-0.26
		Thl	-0.18	-0.06
guaiacol	-0.41	EGB	-0.11	0.01
		Thg	0.16	-0.03
		Thl	-0.10	0.19
isoeugenol	-0.27	EGB	-0.15±0.05	0.05±0.05
		Thg	0.09±0.04	0.00±0.04
		Thl	-0.11	0.13
vanillic acid	-0.47	EGB	-0.32	0.30
		Thg	-0.15	0.08
		Thl	-0.27±0.04	0.14
vanillin	-1.2±0.1	EGB	0.44	-0.71
		Thg	1.10	-0.78
		Thl	0.87	-0.69

**Table 5.3d.** Changes in a\* for MLCs treated with mercaptans and irradiated for 12 hours by Ultravitalux sunlamps.

MLC	<sup>a</sup> reversion: $\Delta a^*$ (12hrs-0hrs)	mercaptan	<sup>b</sup> bleaching: $\Delta a^*$ (treated-untreated)	<sup>c</sup> reversion: $\Delta a^*$ (12hrs-0hrs)
eugenol	-0.1	EGB	-0.1	-0.1
		Thg	-0.4	0.0
		Thl	-0.1	-0.2
guaiacol	0.3	EGB	0.1	0.0
		Thg	-0.1	0.0
		Thl	0.0	-0.1
isoeugenol	0.0	EGB	0.2	-0.3
		Thg	-0.1	0.1
		Thl	0.1	-0.1
vanillic acid	0.0	EGB	0.1	-0.1
		Thg	0.1	-0.2
		Thl	0.1	-0.1
vanillin	-0.1	EGB	0.3	-0.3
		Thg	0.2	-0.4
		Thl	0.3	0.1



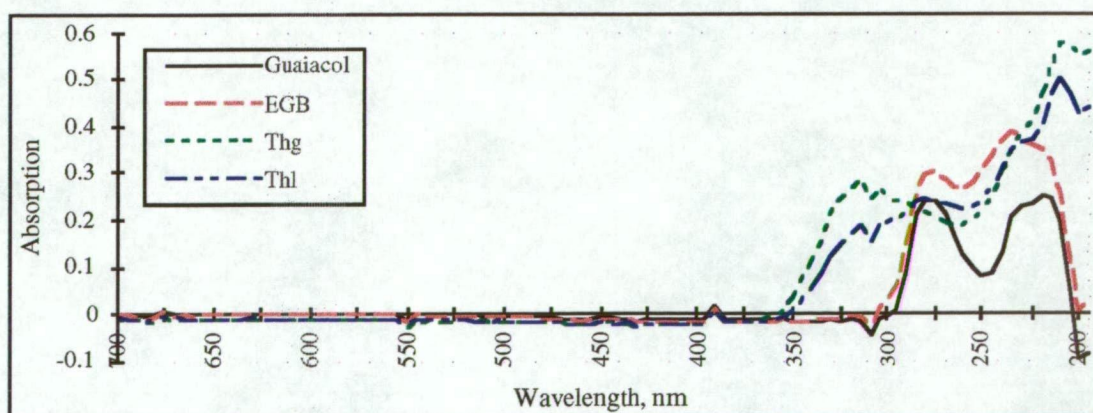
From Tables 5.2 and 5.3, it is apparent that no MLC, except for vanillin, was significantly bleached by any mercaptan (i.e. there were no significant changes in the colour parameters or absorption coefficients after treatment with each mercaptan). This was expected as each MLC was initially colourless. Bleaching was observed for vanillin despite it also being originally colourless. Vanillin is very susceptible to oxidation and a slight pink hue was observed prior to sampling the non-irradiated untreated sample, so atmospheric oxidation could account for an original discolouration. This discolouration was removed by all mercaptans.

Inhibition of reversion was varied, revealing a complete inhibition by all mercaptans for guaiacol, isoeugenol and vanillic acid (i.e. no significant changes in the colour parameters or absorption coefficients after irradiation); a partial inhibition for vanillin (i.e. diminished changes in the colour parameters and absorption coefficients after irradiation, compared to the untreated sample) ; and no inhibition for eugenol (i.e. changes in the colour parameters and absorption coefficients after irradiation were either the same as, or more intense than, those for the untreated sample after irradiation). These results will be discussed below, along with discussions of the changes in the MLCs' UV-visible absorption spectrum after treatment with each mercaptan and subsequent irradiation.

***a. Compounds in which reversion was completely or almost completely inhibited by each mercaptan***

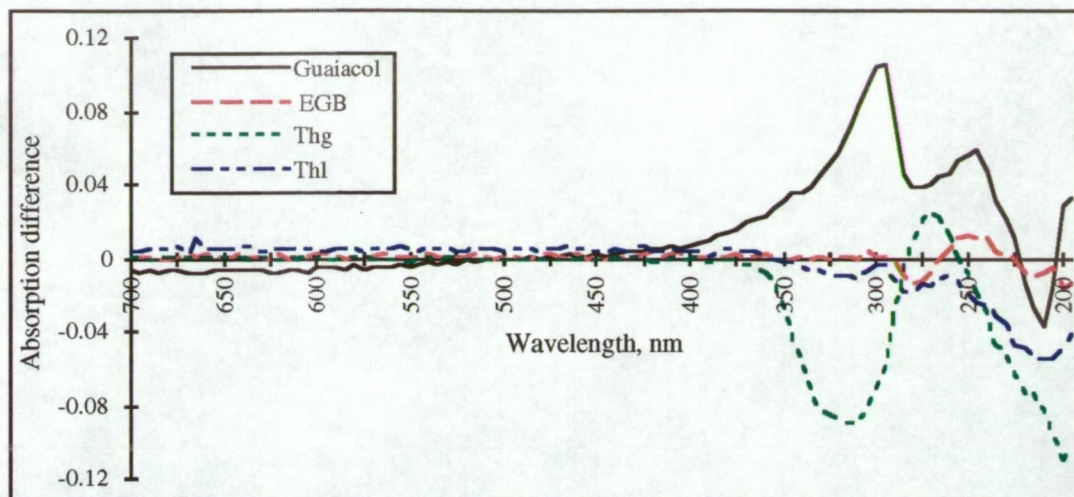
*Guaiacol*

The UV-visible absorption spectra for guaiacol treated with each mercaptan are shown in Figure 5.2a, and the absorption difference spectra for the irradiated samples minus their non-irradiated counterparts are shown in Figure 5.2b.



**Figure 5.2a.** The UV-visible absorption spectra for guaiacol treated with mercaptans.





**Figure 5.2b.** The UV-visible absorption difference spectra, (as irradiated samples minus non-irradiated samples), for guaiacol treated with mercaptans and irradiated for 12 hours by Ultravitalux sunlamps.

**EGB treatment.** Apart from a hyperchromic effect in all the absorption peaks of guaiacol, the absorption spectra for guaiacol treated with EGB did not differ significantly from that of the untreated MLC (see Figure 5.2a). A shouldering peak at 230nm appeared to have undergone a small bathochromic shift to 235nm, but this was probably due to unreacted EGB, as the absorption spectrum for EGB alone (see Figure 5.1) had revealed a broad absorption peak between 220 and 270nm. Thus it appears that EGB had not undergone any significant initial interactions with guaiacol.

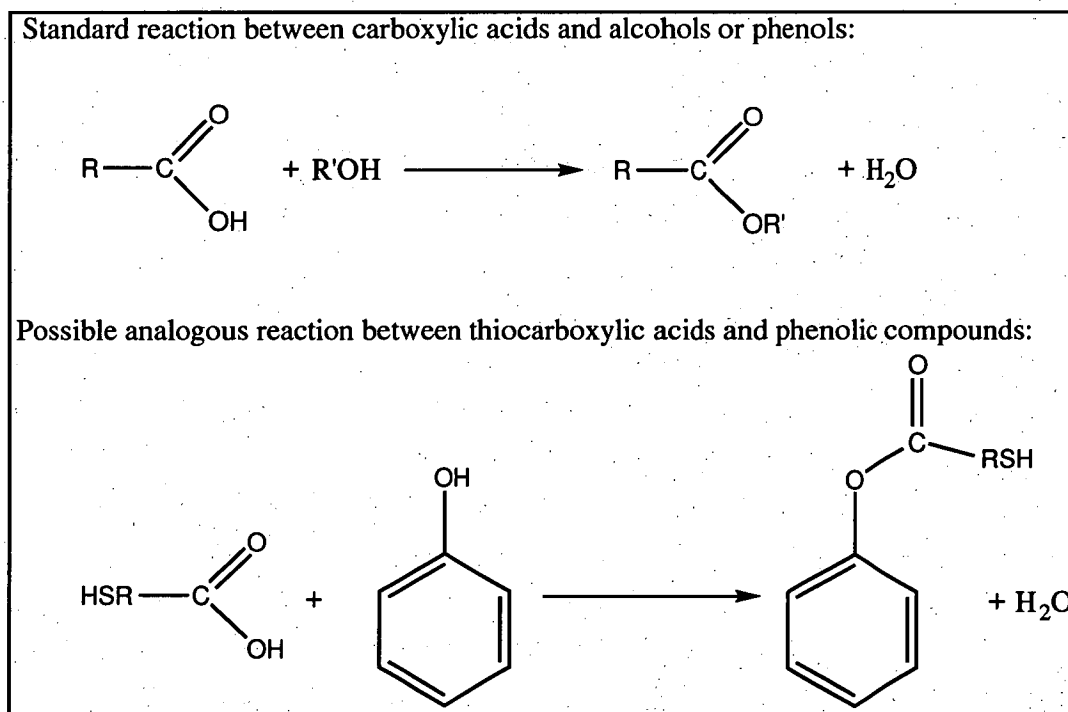
The UV-visible absorption difference spectra for guaiacol treated with EGB and irradiated, (see Figure 5.2b), underwent only minor changes, including small decreases in absorption at 275-280 and 215nm, and a small increase in absorption at 250nm. This increase in absorption coincides with the increase in absorption found for EGB alone (see Figure 5.1), and is therefore possibly due to some photo-activity of EGB (likely to be due to formation of disulphide bonds during ring closure or dimerisation, see Section 5.3.1). The increase in absorption between 300 and 380nm observed for the untreated MLC upon irradiation, (previously attributed to the formation of quinones or other coloured species in Chapter 4), was completely inhibited by the presence of EGB.

Therefore, despite the apparent lack of an interaction between EGB and guaiacol, EGB was still able to completely prevent the formation of photo-induced discolouration products of guaiacol. The lack of an initial interaction suggests that EGB may have inhibited the photo-reversion of guaiacol via ongoing processes, interfering with reversion as it occurred. This could involve several different modes of action, for example:



- a. Removing coloured species, (e.g. quinones), as they were formed.
- b. Acting as a hydrogen donor or radical scavenger, thereby deactivating radical intermediates involved in the discolouration of guaiacol (see Chapter 4).
- c. Shielding guaiacol from UV radiation by acting as a UV-absorber (e.g. the photo-excitation of the C=O groups of EGB and subsequent photo-reactions, see Section 5.3.1, may absorb UV radiation in preference to guaiacol).

**Thg and Thl treatments.** Treatment of guaiacol with Thg and Thl resulted in significant changes in the UV-visible absorption spectrum (Figure 5.2a), which were similar with respect to each other, though that for Thl was less intense. These changes included a large hyperchromic effect at 210nm (due to the COOH group of Thg and Thl), a hyperchromic effect at 235nm, and a large introduction of broad absorption between 295 and 350nm. As these effects were not observed for the EGB treatment, it is possible that the two thiocarboxylic acids had reacted with guaiacol at their COOH groups rather than at their thiol groups. For example, carboxylic acids can react with alcohols or phenols to form esters. Therefore it is possible that the thiocarboxylic acids had reacted with guaiacol in a similar manner, to form an ester. This is shown in Figure 5.3.



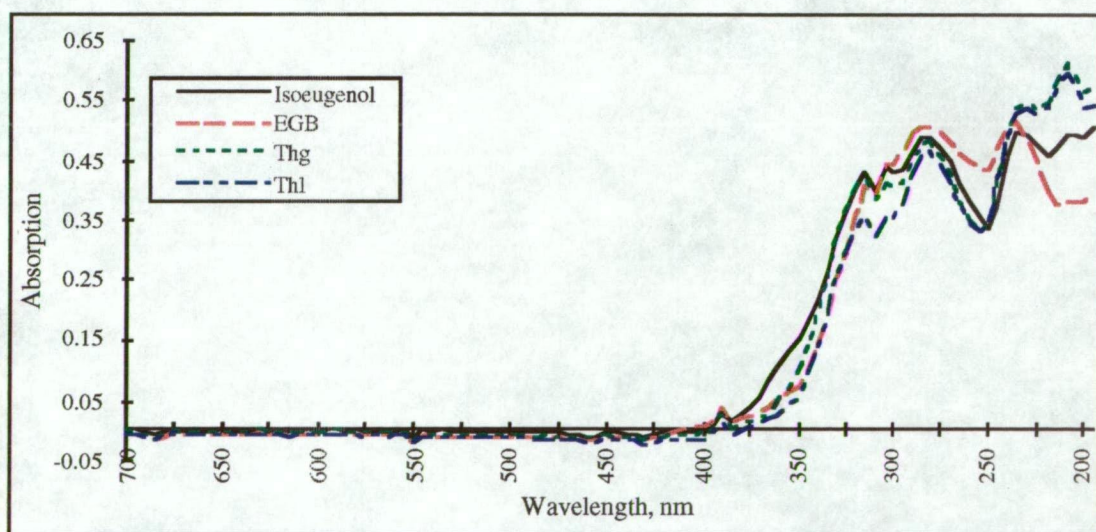
**Figure 5.3.** A possible reaction of thiocarboxylic acids (Thg and Thl) with guaiacol-like compounds, based on standard reactions between carboxylic acids and alcohol or phenol compounds.

The interaction of Thg and Thl shown in Figure 5.3 removes the phenolic hydroxyl group from guaiacol. It was shown in Chapter 4 that this group is necessary for photo-induced reversion to proceed. Therefore Thg and Thl may have inhibited the reversion of guaiacol by effectively modifying the functional group most responsible for reversion. This would result in a true inhibition, whereby yellow products are not removed as they form, but are prevented from forming in the first place. The UV-visible absorption difference spectra for irradiated guaiacol treated with these two mercaptans (Figure 5.2b) support this, as there was no increase in absorption between 300 and 380nm, (previously assigned to the formation of yellow products of irradiated guaiacol in Chapter 4). In fact both mercaptans revealed a decrease in absorption in this region, which was small for Thl but very large for Thg. It is therefore possible that Thg and Thl may also have removed species absorbing between 300 and 380nm (with Thg being more efficient than Thl).

Thus Thg and Thl may have caused at least two inhibitory processes in guaiacol. These could have been an initial reaction with guaiacol (as stated above), which prevented yellowing reactions from occurring, followed by a removal of yellow products formed from residual, or unreacted, guaiacol.

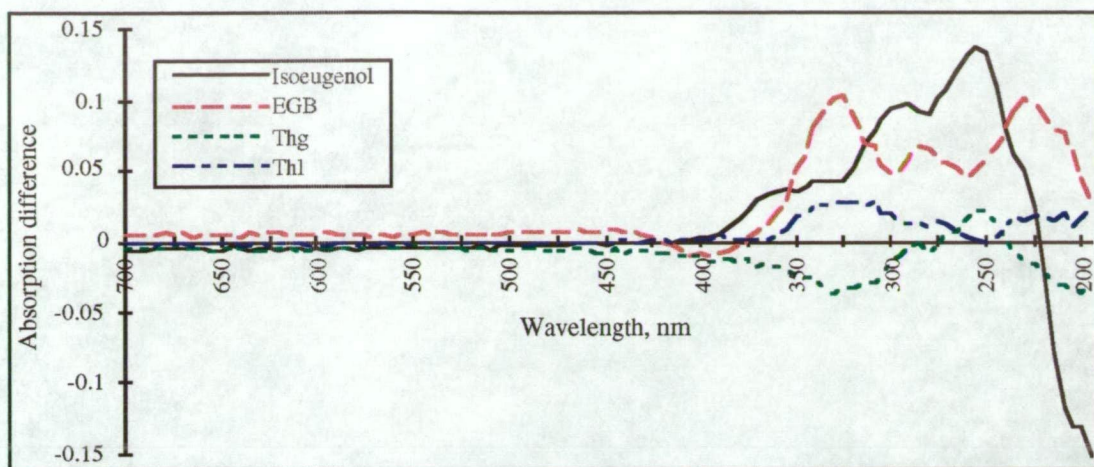
### *Isoeugenol*

The UV-visible absorption spectra for isoeugenol treated with each mercaptan are shown in Figure 5.4a, and the absorption difference spectra for the irradiated samples minus their non-irradiated counterparts are shown in Figure 5.4b



**Figure 5.4a.** The UV-visible absorption spectra for isoeugenol treated with mercaptans.





**Figure 5.4b.** The UV-visible absorption difference spectra, (as irradiated samples minus non-irradiated samples), for isoeugenol treated with mercaptans and irradiated for 12 hours by Ultravitalux sunlamps.

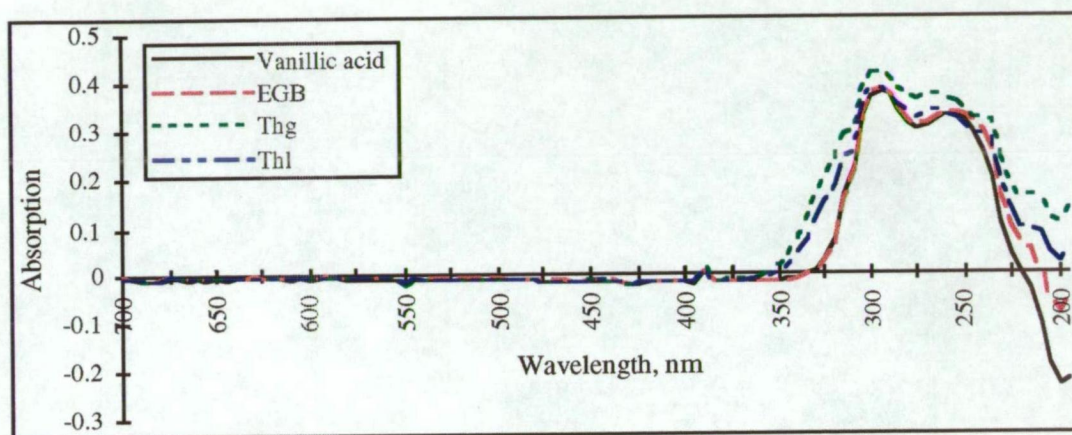
The UV-visible absorption spectra for isoeugenol treated with mercaptans (Figure 5.4a) showed a decrease in absorption at 210nm after treatment with EGB, and an increase at the same wavelength for Thg and Thl treatment. For Thg and Thl, this could have been due to their mere presence (i.e. COOH absorption), and not indicative of any initial interaction. The rest of the spectrum remained essentially unchanged by treatment with each mercaptan. Therefore, there is no strong indication that initial reactions had occurred between the mercaptans and the MLC. For the Thg and Thl treatments, however, their initial interactions which were observed with guaiacol (see above) manifested as changes in the same regions as the absorption peaks for isoeugenol alone. Thus it remains possible that initial interactions between isoeugenol and Thg and Thl may have occurred, similar to those discussed for guaiacol above.

At a first glance it appears that the UV-visible absorption difference spectra for isoeugenol treated with mercaptans underwent several changes upon irradiation (Figure 5.4b). On closer inspection, however, these changes occurred at identical wavelengths to pre-existing peaks in the absorption spectra for the non-irradiated samples (Figure 5.4a). Therefore they represent hyperchromic or hypochromic effects only, and not a production of any new species. Furthermore, the changes observed for the untreated sample upon irradiation in Figure 5.4b were not emulated in the spectra for either of the mercaptan treated and irradiated samples. Thus the UV-visible absorption difference spectra support the *complete inhibition* observed for isoeugenol by treatment with each mercaptan. The mechanisms for this inhibition may be similar to those proposed for guaiacol above, but at this stage there is no real evidence to prove or disprove this.

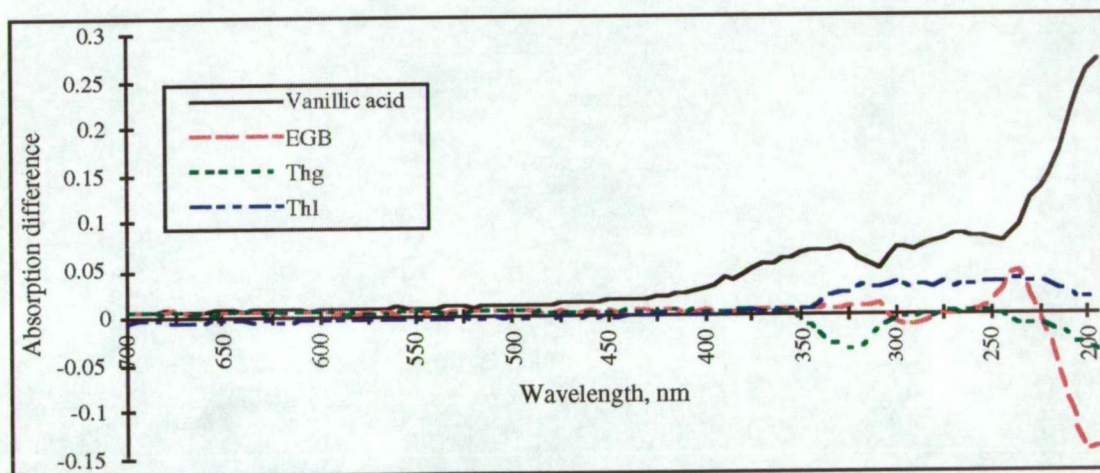


### Vanillic acid

The UV-visible absorption spectra for vanillic acid treated with each mercaptan are shown in Figure 5.5a, and the absorption difference spectra for the irradiated samples minus their non-irradiated counterparts are shown in Figure 5.5b.



**Figure 5.5a.** The UV-visible absorption spectra for vanillic acid treated with mercaptans.



**Figure 5.5b.** The UV-visible absorption difference spectra, (as irradiated samples minus non-irradiated samples), for vanillic acid treated with mercaptans and irradiated for 12 hours by Ultravitalux sunlamps.

The UV-visible absorption spectra for vanillic acid treated with mercaptans (Figure 5.5a) revealed similar effects to those discussed for guaiacol above. That is, EGB treatment had an insignificant effect on the absorption spectrum, while Thg and Thl treatment resulted in absorption between 295 and 350nm. Therefore Thg and Thl may have reacted with vanillic acid in a similar manner to their interaction with guaiacol, destroying the phenolic hydroxyl group and arresting reversion at an early

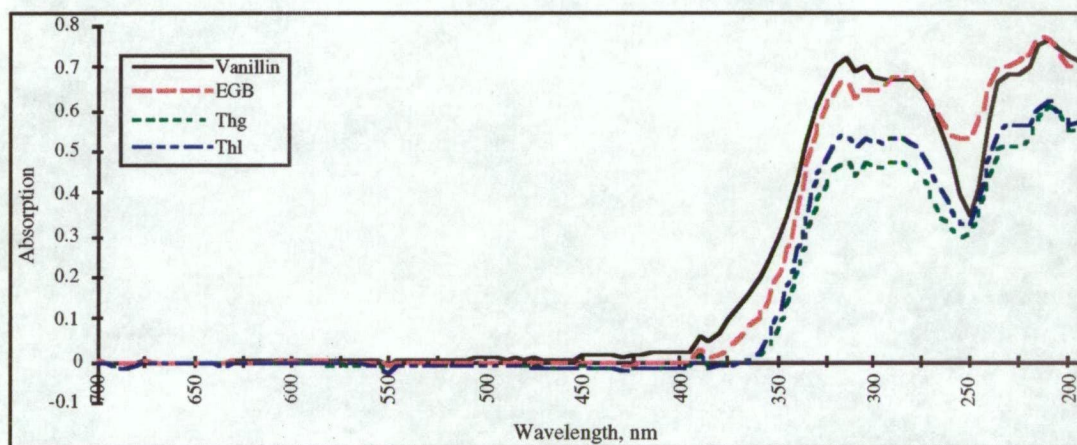


stage. EGB, on the other hand, possibly did not react with vanillic acid, so its inhibitory action was possibly a result of ongoing processes.

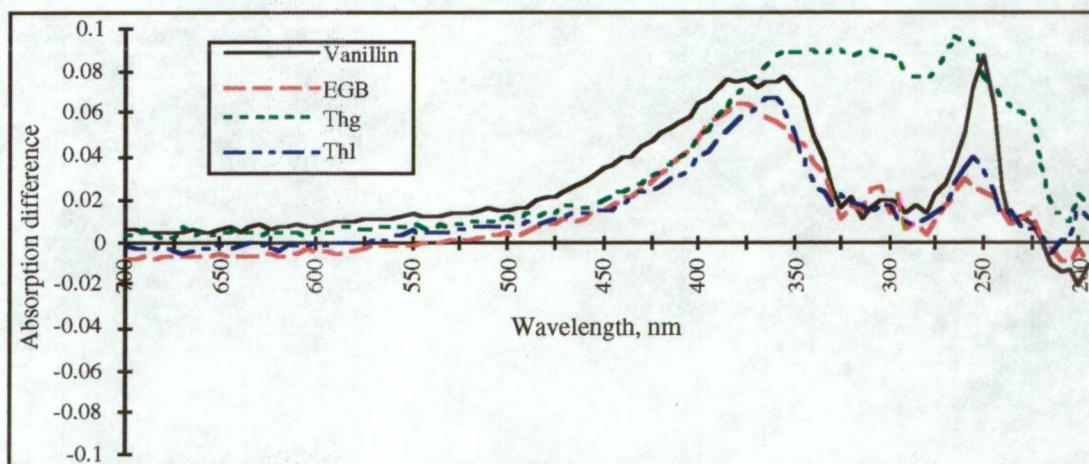
The UV-visible absorption difference spectra for vanillic acid treated with Thg and Thl and irradiated (Figure 5.5b) revealed no significant changes, confirming the total inhibition of reversion observed for these two mercaptans. For the EGB treated sample, the UV-visible absorption spectra underwent only minor changes upon irradiation, which were similar to those already discussed for guaiacol above. Thus, EGB may have inhibited the reversion of vanillic acid exactly as it did for guaiacol.

### ***b. Partial inhibition by each mercaptan (vanillin)***

The UV-visible absorption spectra for vanillin treated with each mercaptan are shown in Figure 5.6a, and the absorption difference spectra for the irradiated samples minus their non-irradiated counterparts are shown in Figure 5.6b



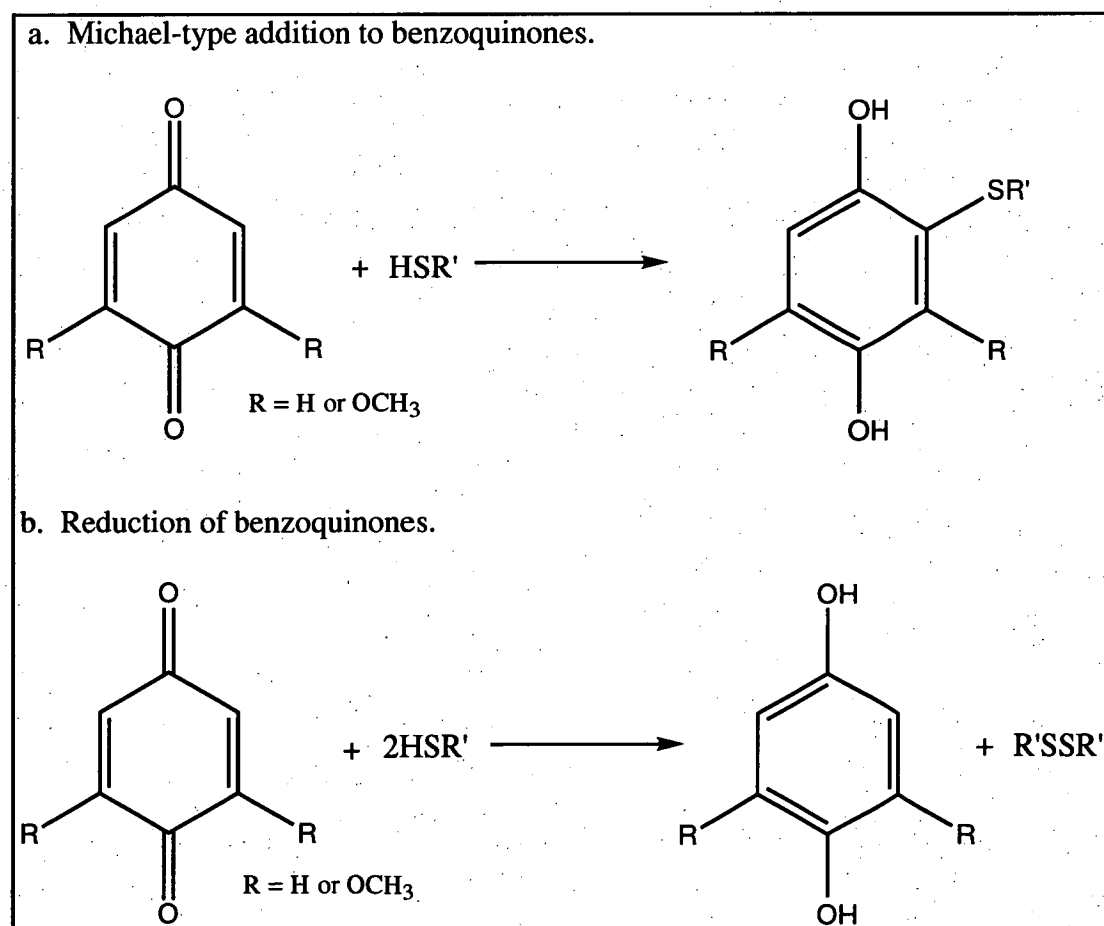
**Figure 5.6a.** The UV-visible absorption spectra for vanillin treated with mercaptans.



**Figure 5.6b.** The UV-visible absorption difference spectra, (as irradiated samples minus non-irradiated samples), for vanillin treated with mercaptans and irradiated for 12 hours by Ultravitalux sunlamps.

The UV-visible absorption spectra for vanillin (Figure 5.6a) revealed a cancellation of absorption above 360nm for both Thg and Thl treatments, and a decrease in this same region for EGB treatment. This region is characteristic of absorption by quinone species, which are formed on oxidation of vanillin (see Chapter 4). As previously mentioned, vanillin had developed a small pink colouration due to atmospheric oxidation prior to treatment and irradiation. The colour parameters revealed that this discolouration was removed on treatment with each mercaptan. This is consistent with the observations of the absorption spectra, indicating that the oxidation product was indeed a quinone species, and that it was removed, or at least partially removed, by each mercaptan.

Thiol compounds are able to remove quinone species through Michael-type addition of the thiol onto the quinone<sup>71,97</sup>, or by reducing the quinone to its hydroquinone counterpart<sup>71,101</sup>. These reactions have been shown to occur simultaneously for several methoxyl-substituted-*p*-quinones, with the resultant yield favouring the Michael-type addition reaction (cited by Hirashima and Sumimoto<sup>71</sup>). Therefore it is likely that the quinone species in the oxidised vanillin sample were also removed through Michael-type addition reactions and reduction to hydroquinones. These two reactions are shown in Figure 5.7.

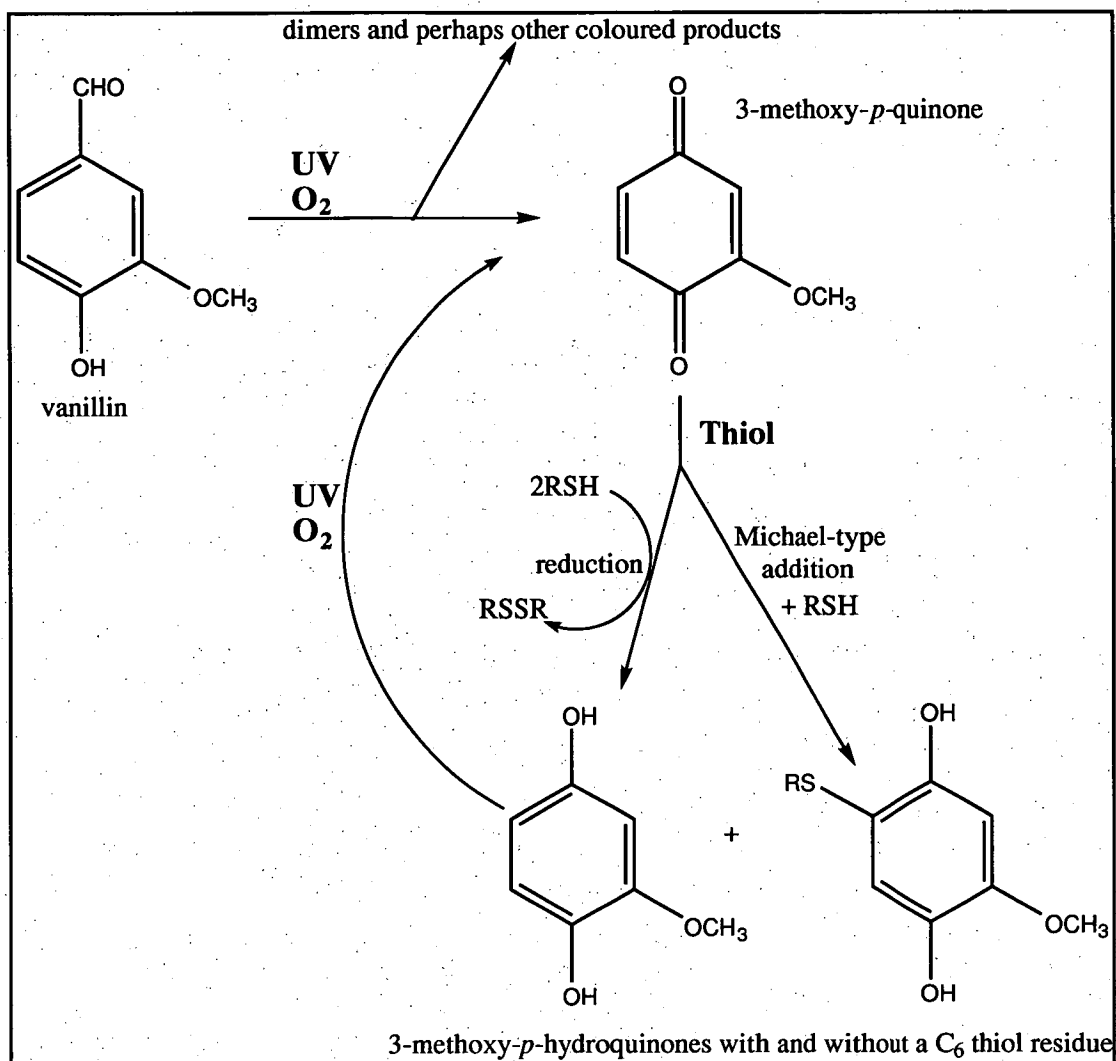


**Figure 5.7.** Destruction of quinone species by thiols<sup>71,97,101</sup>.

No other significant changes (aside from differing intensities) were observed in the absorption spectra for vanillin upon treatment with each of the mercaptans. Therefore, besides the removal of the quinone oxidation product, it appears that no mercaptan had an initial interaction with vanillin. It should be noted, though, that the spectral regions found to have been altered by Thg and Thl treatment of guaiacol (see Figure 5.2a) were masked by the large absorption peak for vanillin alone in Figure 5.6a. Thus it is possible that Thg and Thl may still have reacted with vanillin in a similar manner to their initial reactions with guaiacol, discussed above.

The UV-visible absorption difference spectra of vanillin treated with the mercaptans (Figure 5.6a) revealed that the samples treated with EGB and Thl both underwent similar spectral changes upon irradiation to the changes that were observed for the untreated MLC. The intensities of the absorption peaks were, however, lower for the treated samples. Included in these spectral changes was the introduction of, or increase in, absorption at 360nm, which tailed to about 600nm. This is characteristic of the formation of quinone species, as previously shown in Chapter 4. The Thg treated sample also revealed a reduction in absorption in this area. Differing from the other mercaptans, though, treatment with Thg also resulted in a hyperchromic effect between 220 and 360nm. This was not likely to have been a result of the introduction of a new species, however, as this spectral region was already present in the non-irradiated sample. Therefore each mercaptan treatment of vanillin resulted in a reduction of the quinone products formed by irradiation. Their production was not, however, completely inhibited.

It is possible that the mercaptans removed the products of irradiation (i.e. quinones, see Chapter 4) as they were formed, probably via the mechanisms shown in Figure 5.7. The mercaptan-reduced quinones may then have undergone subsequent photo-induced oxidation, reforming the original quinone species. A reduction-oxidation cycle could then have been established, resulting in a gradual depletion of reactive thiol groups. The rate of quinone formation may also have exceeded that of their removal by mercaptans, giving an overall effect of only a partial degree of inhibition. This is outlined in Figure 5.8.

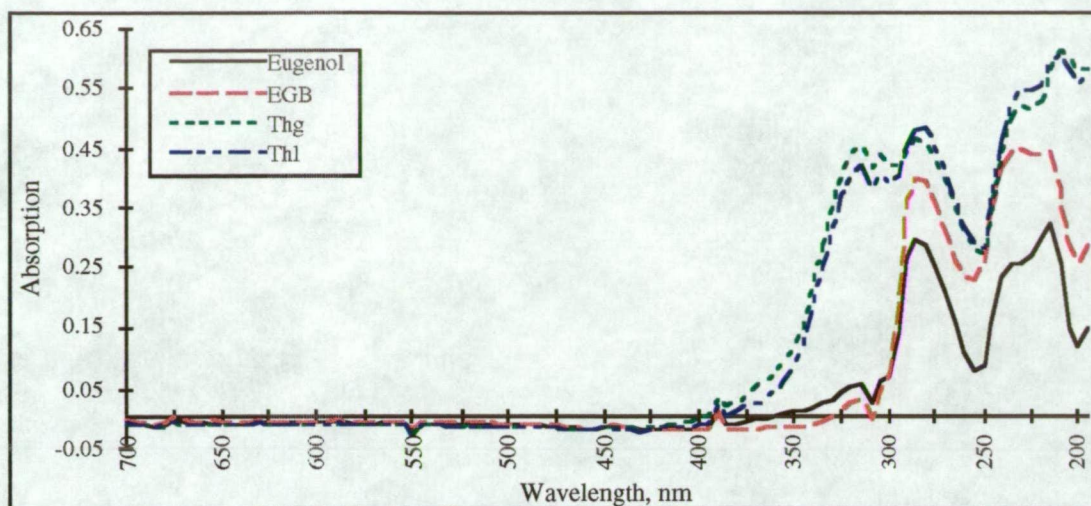


**Figure 5.8.** A possible mechanism for the photo-induced reversion of vanillin and its inhibition by mercaptans, or thiols. The cycling of the mercaptan-reduction of coloured quinones and their photo-oxidative reformation could gradually lead to a depletion of active thiol groups, resulting in an overall inefficiency in inhibition.

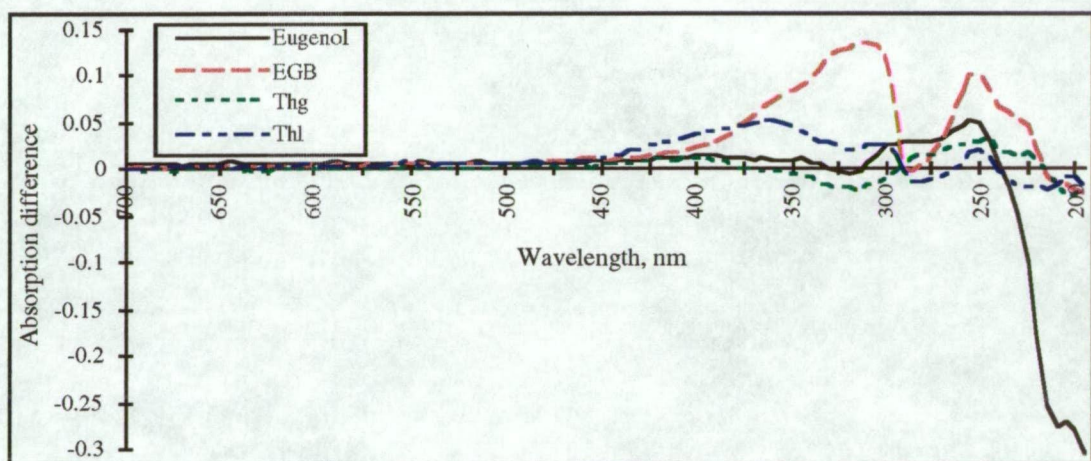
### *c. No inhibition for each mercaptan (eugenol)*

Changes in the absorption coefficients and tristimulus colour parameters upon irradiation of the mercaptan treated samples were not significantly different from those incurred for untreated eugenol irradiated for 12 hours. Therefore, no mercaptan was able to inhibit the photo-induced discolouration of eugenol. In fact, for Thl treated samples the increase in  $b^*$  (or yellowing) was greater than that for the untreated sample. Therefore it appears that Thl has not only failed to inhibit reversion, but has actually increased it slightly. The UV-visible absorption spectra for eugenol treated with each mercaptan are shown in Figure 5.9a, and the absorption difference spectra for the irradiated samples minus their non-irradiated counterparts are shown in Figure 5.9b.





**Figure 5.9a.** The UV-visible absorption spectra for eugenol treated with mercaptans.



**Figure 5.9b.** The UV-visible absorption difference spectra, (as irradiated samples minus non-irradiated samples), for eugenol treated with mercaptans and irradiated for 12 hours by Ultravitalux sunlamps.

The UV-visible absorption spectra for eugenol treated with mercaptans (Figure 5.8a) revealed that each mercaptan had imparted identical changes to those already discussed for guaiacol above. Therefore it appears that eugenol, like guaiacol, had not interacted with EGB, but had interacted with both Thg and Thl.

The UV-visible absorption difference spectra for irradiated eugenol (Figure 5.8b) revealed a very weak and broad increase in absorption between 335 and 450nm (probably due to the production of quinone species, see Chapter 4), a large decrease in absorption between 205-215nm (possibly due to photo-activity of the C=C bond in the 3-carbon side chain, see Chapter 4), and a small hyperchromic effect between 250 and 285nm. Apart from the decrease in absorption at 205-215nm, treatment with each mercaptan had also resulted in the above changes, with differing intensities. No

mercaptan-treated sample experienced a depletion of absorption between 205 and 215nm. As this region is consistent with absorption by mercaptans alone (see Figure 5.1), the presence of the mercaptans may have masked any depletion in absorption in this area resulting from irradiated eugenol. The increases in absorption seen at 225 and 250nm, particularly for the EGB treated sample, may simply have been due to the presence of the mercaptans. The increases in absorption above 300nm, however, could not have been due to mercaptans alone, as this region is beyond the absorption range seen for the mercaptans (see Figure 5.1).

The broad peak at 335-450nm was not prevented from being formed by both Thg and Thl treatments. In fact, its formation was equal to that of eugenol alone for the Thg treated sample, and markedly elevated for the Thl treated sample. This indicates that the presence of Thg had not affected the formation of quinone species in irradiated eugenol, while the presence of Thl had enhanced the formation of quinone species. (This is consistent with the unchanged yellowing (i.e. similar increase in  $b^*$ ) for the Thg treatment, and the elevated yellowing (i.e. elevated increase in  $b^*$ ) for the Thl treatment, compared to the untreated and irradiated eugenol sample shown in Table 5.3b). It is unclear as to why this was, as it certainly did not occur for treated and irradiated guaiacol, nor did it occur for isoeugenol (which is identical to eugenol except that its 3-carbon side chain  $C=C$  bond is at the  $\alpha$ - $\beta$  position rather than the  $\beta$ - $\gamma$  position). It could be that:

- a. Thg and Thl had not attached to (and therefore not deactivated) the phenolic hydroxyl group, which was suggested for guaiacol above;
- b. They attached to the phenolic hydroxyl group, but at such a slow rate that unreacted eugenol was still present. The Thg-eugenol and Thl-eugenol complexes may then have photo-sensitised, or otherwise enhanced, the photo-induced production of quinones from the residual eugenol. Thl, in particular, may also have enhanced other photo-yellowing reactions (as the increase in absorption between 240 and 300nm for the Thl treated sample was *less than* that for the untreated sample, while the increase in absorption above 300nm for the treated sample was *greater than* that for the untreated sample).
- c. The presence of a 3-carbon side chain  $C_\beta=C_\gamma$  bond may have altered the reactions of the mercaptans.

The UV-visible absorption difference spectrum for eugenol treated with EGB and irradiated (Figure 5.8) suggests that EGB had again acted differently from Thg and Thl. While quinone species were still produced in the presence of EGB (indicated by the absorption peak at about 425nm and the shoulder at 360nm), it appears that a new species, absorbing between 300 and 330nm, was also produced. This is evidenced

by the large increase in absorption centred around 320nm for the EGB treated sample upon irradiation, which was not observed in the spectra for the other samples. Again it is unclear why eugenol behaved differently from guaiacol or isoeugenol in the presence of EGB. It is possible that while EGB may inhibit some photo-yellowing reactions, it also strongly catalyses others.

### *Summary for Category 2 compounds*

The ability of mercaptans to inhibit the photo-induced reversion of Category 2 MLC compounds was varied. Of the five MLCs in this category, three were completely inhibited (guaiacol, isoeugenol and vanillic acid) while the remaining two experienced little (vanillin) or no inhibition (eugenol) by each mercaptan.

No structural trends previously discussed in Chapter 4 could account for this observation, as the three compounds which experienced inhibition had different functional groups (guaiacol contained no other groups apart from the phenolic hydroxyl and methoxyl group common to all, isoeugenol contained a 3-carbon side chain  $C_{\alpha}=C_{\beta}$  bond, and vanillic acid contained a COOH ring-substituent).

It appeared that while Thg and Thl may have exhibited similar modes of activity, EGB acted via different mechanisms.

For the MLCs which experienced complete inhibition, no initial interaction between EGB and the MLC was supported. This suggests that EGB inhibited throughout irradiation (for example, it may have removed coloured species as they were formed).

Thg and Thl, on the other hand, did appear to have undergone an initial interaction with these MLCs, possibly via reaction at the COOH groups of these two mercaptans. This initial reaction may have deactivated the phenolic hydroxyl groups, thereby truly preventing reversion from occurring.

Each mercaptan was able to remove a quinone contaminant (introduced via atmospheric oxidation) from the vanillin sample. This was likely to have occurred via simultaneous reductions by the mercaptans, and Michael-type additions of the mercaptans. These reactions may have introduced a highly reactive hydroxyquinone species into the sample, which photo-oxidised and set-up a mercaptan-reduction / photo-oxidation

cycle. The mercaptans may have then been gradually depleted during these cycles, resulting in inefficient inhibition overall.

Eugenol was the only compound in this category that did not experience any inhibition of reversion by the mercaptans. It is unclear why this was. It is possible that the mercaptans still behaved as inhibitors for some photo-reactions of eugenol, but sensitised or catalysed other reactions that were otherwise minor.

#### 5.3.4 Category 3 compounds: Reversion with a change in the red-green colour coordinate $a^*$

The observations of colour changes upon treatment with mercaptans and subsequent irradiation by Ultravitalux sunlamps for 12 hours are shown in Table 5.4 for MLCs previously determined in Chapter 4 as belonging to Category 3. Changes in the absorption coefficients and tristimulus colour parameters are shown in Tables 5.5a-d. Again, the changes incurred in the colour parameters for the untreated samples (from Chapter 4) on irradiation have been included in these tables to aid in comparisons.

**Table 5.4.** Observations of the colour of MLC solutions treated with mercaptans and irradiated for 12 hours by Ultravitalux sunlamps.

MLC	original	irradiated	mercaptan	treated	treated and irradiated
methoxy-hydroquinone	orange-brown	orange-red	EGB	brown tinge	dark orange
			Thg	pale brown	pale orange
			Thl	pale brown	brown
methyl-hydroquinone	colourless	light orange-pink	EGB	colourless	dark orange
			Thg	colourless	colourless
			Thl	colourless	orange tinge
syringaldehyde	yellow tinge	light orange-yellow	EGB	yellow tinge	light orange
			Thg	colourless	orange
			Thl	colourless	dark orange

**Table 5.5a.** Changes in the absorption coefficients,  $k$  ( $\text{g/m}^2$ )<sup>-1</sup>, for MLCs treated with mercaptans and irradiated for 12 hours by Ultravitalux sunlamps.

MLC	<sup>a</sup> reversion: $\Delta k_{(12\text{hrs}-0\text{hrs})}$	mercaptan	<sup>b</sup> bleaching: $\Delta k_{(\text{treated}-\text{untreated})}$	<sup>c</sup> reversion: $\Delta k_{(12\text{hrs}-0\text{hrs})}$
methoxy-hydroquinone	11.9±0.8	EGB	-17.4±0.3	0.7
		Thg	-6.5±0.3	1.1±0.2
		Thl	-13.6±0.3	19.2±0.6
methyl-hydroquinone	3.7	EGB	-0.3	9.5
		Thg	-0.5	4.2
		Thl	-0.4	5.4
syringaldehyde	5.0	EGB	-0.6	3.5
		Thg	-0.9	4.6
		Thl	-0.8	6.2

Note that standard deviations are ±0.1 unless stated otherwise. <sup>a</sup>Reversion of the untreated MLCs, reviewed from Chapter 4. <sup>b</sup>Bleaching effect of mercaptans on MLCs is indicated by a decrease in  $k$  on treatment. <sup>c</sup>Reversion or increase in  $k$  of the MLCs treated with mercaptans.

**Table 5.5b.** Changes in  $b^*$  for MLCs treated with mercaptans and irradiated for 12 hours by Ultravitalux sunlamps.

MLC	<sup>a</sup> reversion: $\Delta b^*_{(12\text{hrs}-0\text{hrs})}$	mercaptan	<sup>b</sup> bleaching: $\Delta b^*_{(\text{treated}-\text{untreated})}$	<sup>c</sup> reversion: $\Delta b^*_{(12\text{hrs}-0\text{hrs})}$
methoxy-hydroquinone	1.5	EGB	-6.0	0.8
		Thg	-0.1	0.7
		Thl	-2.7	2.9
methyl-hydroquinone	2.3	EGB	-0.1	4.7
		Thg	-0.6	3.5
		Thl	-0.6	4.3
syringaldehyde	4.7	EGB	-1.1	4.3
		Thg	-1.3	4.8
		Thl	-1.3	5.9

Note that standard deviations are ±0.1 unless stated otherwise. <sup>a</sup>Reversion of the untreated MLCs, reviewed from Chapter 4. <sup>b</sup>Bleaching effect of mercaptans on MLCs is indicated by a decrease in  $b^*$  on treatment. <sup>c</sup>Reversion or increase in  $b^*$  of the MLCs treated with mercaptans.

**Table 5.5c.** Changes in L\* for MLCs treated with mercaptans and irradiated for 12 hours by Ultravitalux sunlamps.

MLC	<sup>a</sup> reversion: $\Delta L^*_{(12\text{hrs}-0\text{hrs})}$	mercaptan	<sup>b</sup> bleaching: $\Delta L^*_{(\text{treated}-\text{untreated})}$	<sup>c</sup> reversion: $\Delta L^*_{(12\text{hrs}-0\text{hrs})}$
methoxy-hydroquinone	$-2.70 \pm 0.06$	EGB	$5.46 \pm 0.05$	-0.05
		Thg	$3.16 \pm 0.05$	0.15
		Thl	$4.91 \pm 0.05$	$-5.16 \pm 0.04$
methyl-hydroquinone	-1.73	EGB	0.14	-3.28
		Thg	$0.30 \pm 0.04$	$-1.63 \pm 0.04$
		Thl	$0.18 \pm 0.04$	$-1.80 \pm 0.04$
syringaldehyde	-0.99	EGB	0.15	-0.76
		Thg	$0.4 \pm 0.1$	$-1.1 \pm 0.1$
		Thl	0.22	-1.17

Note that standard deviations are  $\pm 0.02$  unless stated otherwise. <sup>a</sup>Reversion of the untreated MLCs, reviewed from Chapter 4. <sup>b</sup>Bleaching effect of mercaptans on MLCs is indicated by an increase in L\* on treatment. <sup>c</sup>Reversion or decrease in L\* of the MLCs treated with mercaptans.

**Table 5.5d.** Changes in a\* for MLCs treated with mercaptans and irradiated for 12 hours by Ultravitalux sunlamps.

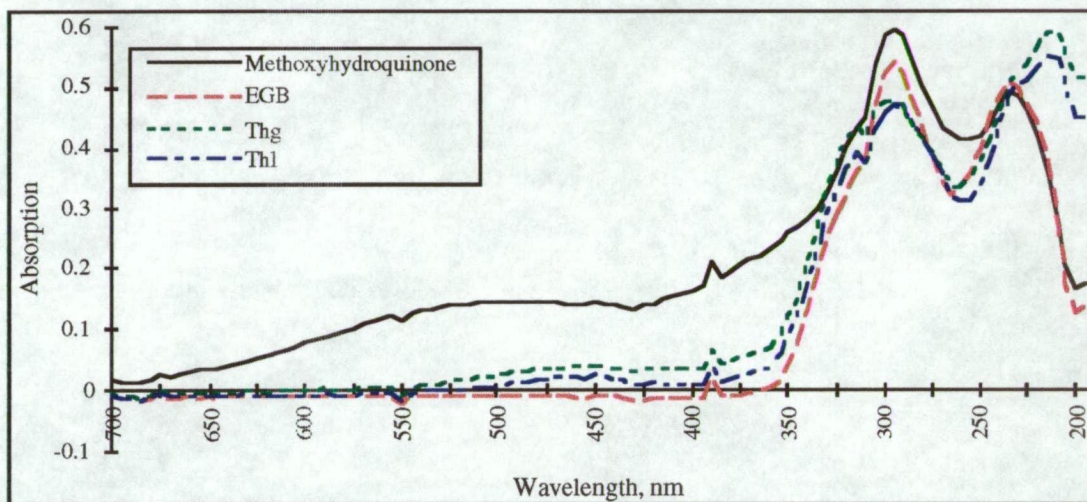
MLC	<sup>a</sup> reversion: $\Delta a^*_{(12\text{hrs}-0\text{hrs})}$	mercaptan	<sup>b</sup> bleaching: $\Delta a^*_{(\text{treated}-\text{untreated})}$	<sup>c</sup> reversion: $\Delta a^*_{(12\text{hrs}-0\text{hrs})}$
methoxy-hydroquinone	2.3	EGB	-2.8	-0.2
		Thg	-1.9	0.0
		Thl	-3.1	4.0
methyl-hydroquinone	1.1	EGB	-0.2	1.5
		Thg	-0.3	0.4
		Thl	-0.2	0.2
syringaldehyde	-0.7	EGB	0.1	-0.5
		Thg	0.0	-0.4
		Thl	0.1	-0.5

Note that standard deviations are  $\pm 0.1$  unless stated otherwise. <sup>a</sup>Reversion of the untreated MLCs, reviewed from Chapter 4. <sup>b</sup>Bleaching effect of mercaptans on MLCs is indicated by a decrease in a\* on treatment. <sup>c</sup>Reversion or increase in a\* of the MLCs treated with mercaptans.

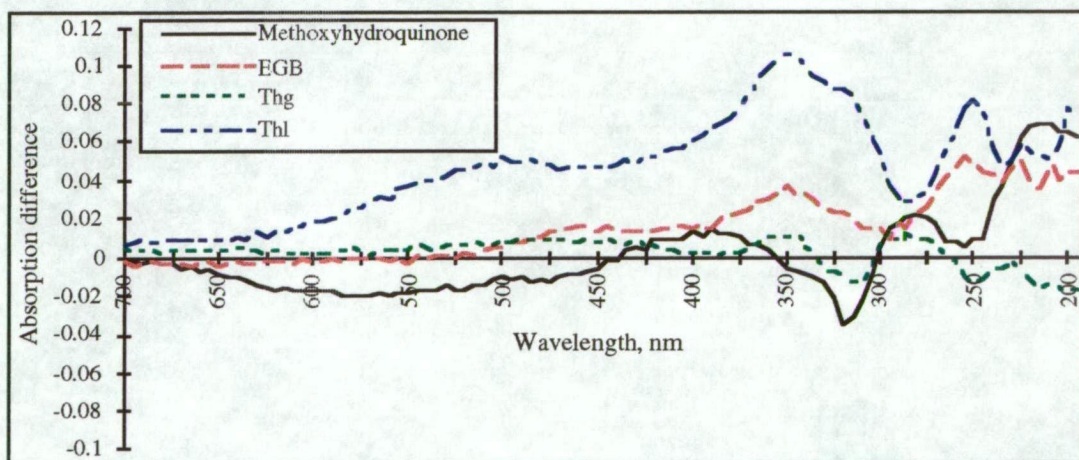


*a. quinone species*

The UV-visible absorption spectra for methoxyhydroquinone and methylhydroquinone treated with mercaptans are shown in Figures 5.10a and 5.11a, and the absorption difference spectra for these samples after irradiation are shown in Figures 5.10b and 5.11b, respectively.

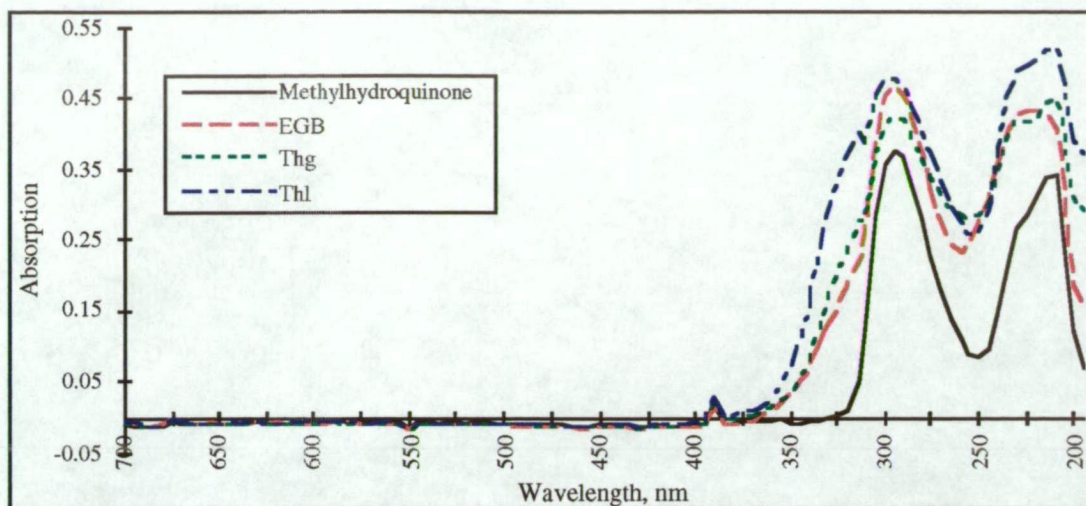


**Figure 5.10a.** The UV-visible absorption spectra for methoxyhydroquinone treated with mercaptans.

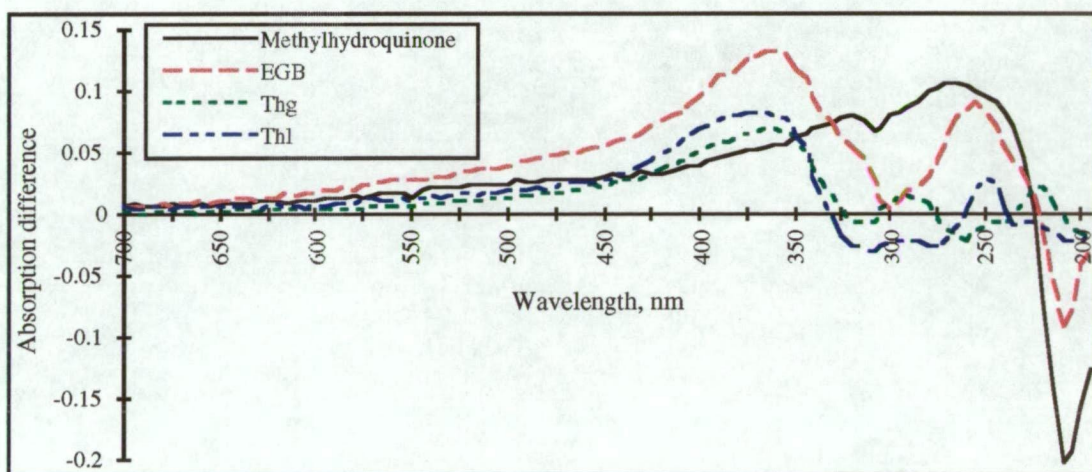


**Figure 5.10b.** The UV-visible absorption difference spectra, (as irradiated samples minus non-irradiated samples), for methoxyhydroquinone treated with mercaptans and irradiated for 12 hours by Ultravitalux sunlamps.





**Figure 5.11a.** The UV-visible absorption spectra for methylhydroquinone treated with mercaptans.



**Figure 5.11b.** The UV-visible absorption difference spectra, (as irradiated samples minus non-irradiated samples), for methylhydroquinone treated with mercaptans and irradiated for 12 hours by Ultravitalux sunlamps.

### *Methoxyhydroquinone*

**Bleaching by mercaptans.** For methoxyhydroquinone, bleaching was extensive for all mercaptans, as revealed by observed colour changes along with changes in the absorption coefficients and colour parameters in Tables 5.4 and 5.5. EGB was slightly better than Thl, and much more efficient than Thg. The UV-visible absorption spectra in Figure 5.10a showed that EGB had removed all absorption above 360nm, while Thl and Thg had diminished it greatly. The peak at 300nm was also diminished, and a 210-215nm peak was introduced by treatment with Thg and Thl. This latter peak can be attributed to the presence of these two mercaptans alone,



as it overlaps with absorption of Thg and Thl alone (see guaiacol, Category 2 compounds).

As mentioned in Chapter 4, the non-irradiated methoxyhydroquinone sample consisted of both methoxyhydroquinone and methoxyquinone species, established as a redox system due to atmospheric oxidation. The removal of all absorption above 360nm in Figure 5.10a indicates that each mercaptan had removed the coloured methoxyquinone species, hence the observed bleaching effect. It is likely that this proceeded via reduction and Michael-type addition reactions, as shown previously in Figure 5.7.

**Inhibition of reversion.** Upon irradiation, observations of colour changes, along with changes in the absorption coefficients and colour parameters shown in Tables 5.4 and 5.5, revealed that EGB had inhibited the reversion of methoxyhydroquinone greatly, and Thg only slightly less, while Thl had increased reversion.

The UV-visible absorption difference spectra for irradiated methoxyhydroquinone (Figure 5.10b) revealed changes that were inconsistent with those normally indicative of reversion. For example, there was a small but broad decrease in absorption in the visible region (between 440 and 660nm), which implies a removal of colouration rather than an increase in it. It was proposed in Chapter 4 that the irregular spectrum for irradiated methoxyhydroquinone could have been a result of interferences between reaction components of the opposing redox partners present in the sample, creating an overall cancellation effect. The difference spectra for each mercaptan treated sample will therefore be discussed on their own merit rather than by comparing them to the spectra for the untreated MLC.

For each mercaptan-treated sample, absorption increased around 360 and 450nm. This is indicative of the formation of quinone species, and was very weak for the EGB treated sample, and moderately weak for the Thg treated sample. This supports the observations presented in Tables 5.4 and 5.5, that both the EGB treatment and the Thg treatment had resulted in a very good inhibition (although not complete), with EGB being the more efficient of the two. The difference spectra for methoxyhydroquinone treated with Thl and irradiated revealed a very large increase in quinone production (i.e. large increases in absorption at 360 and 450nm), as well as dimerisation and/or cyclisation products of these quinones (i.e. a large increase in absorption around 525nm, see Chapter 4).

The inhibition of reversion in this case could also have proceeded via the mechanism proposed for vanillin and shown in Figure 5.8. The reduction-oxidation cycling in this mechanism would explain the incomplete inhibition of reversion for methoxyhydroquinone. The different efficiencies observed for each mercaptan could

have resulted from different reaction rates, and also different proportions of reduction to Michael-type addition products, which in turn could exhibit differing rates of re-oxidation. For example, the removal of quinone species by EGB (and Thg) may have been faster and more favourable than photo-induced reformation reactions for the same compound. Therefore, the EGB-quinone-hydroquinone system would exhibit less discolouration after irradiation. Thl-induced reduction, on the other hand, may have been slower than photo-oxidation, resulting in an inefficient prevention of discolouration.

Alternatively, EGB and Thg may have initially bleached, or removed, the quinone species via an irreversible process, thereby disabling their photo-oxidative re-introduction. Thl treatment, on the other hand, which resulted in less initial bleaching, may have involved a reversible process, such that yellow species were easily re-formed.

### *Methylhydroquinone*

Methylhydroquinone was originally colourless, so no bleaching was observed for the absorption coefficients or the colour parameters presented in Tables 5.4 and 5.5. Despite this, the UV-visible absorption spectra (Figure 5.11a) revealed that interactions may still have occurred with each mercaptan, as each treatment resulted in an introduction of absorption between 320 and 360nm. This is similar to the effect Thg and Thl treatment had on guaiacol (see Figure 5.2a), so it is possible that Thg and Thl reacted with methylhydroquinone as they did with guaiacol, discussed in Category 1 compounds.

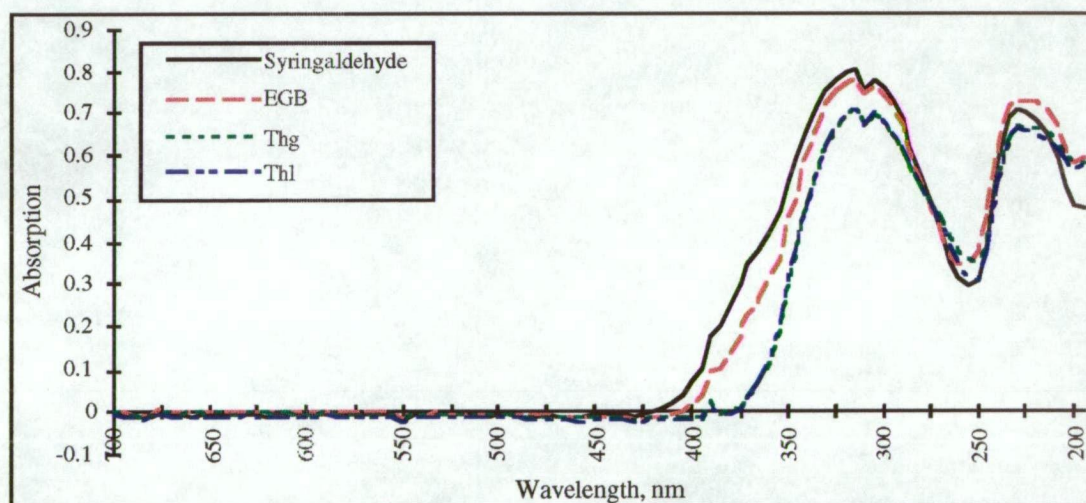
For methylhydroquinone, inhibition was varied for the three mercaptans, with erratic results. Visually it appeared that Thg had completely inhibited reversion, Thl had largely inhibited reversion and EGB had actually increased reversion (Table 5.4). The changes in the absorption coefficients and colour parameters after irradiation (Tables 5.5), however, indicated that all three mercaptan treatments had increased reversion, Thg and Thl only slightly and EGB greatly. It is possible that Thg and Thl were able to inhibit reversion reactions via ongoing processes during irradiation, but had lost their inhibition ability when irradiation ceased. When irradiated treated samples were stored, prior to taking their measurements, post-storage-reversion may have occurred to an elevated degree.

The UV-visible absorption difference spectra (see Figure 5.11b) revealed that the EGB treated sample had lost the 215nm peak upon irradiation, while a large amount of absorption was introduced beyond 300nm, tailing well into the visible region (up to 600nm), which represents the formation of coloured species. In Thg and Thl

treated samples, absorption was also introduced above 300nm, which tailed into the visible region, but less so than for the EGB treated sample. This spectral region is typical of absorption by quinone species (and their dimerisation/cyclisation products), so it is apparent that initial interactions between the mercaptans and methylhydroquinone had not prevented the photo-induced quinone formation at all. In fact, the presence of EGB in particular seems to have aided this formation.

### ***b. Syringaldehyde***

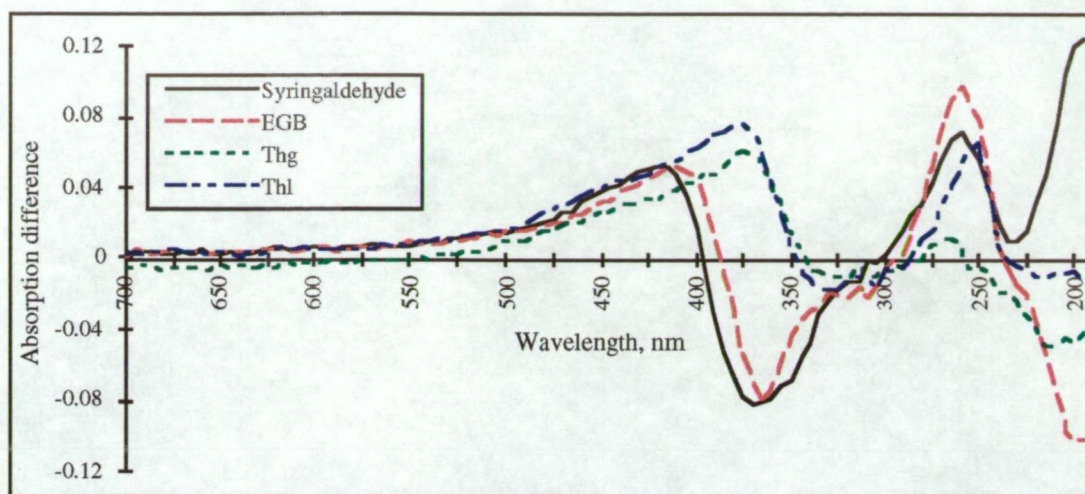
Bleaching was observed on treatment of syringaldehyde with all three mercaptans, as revealed by changes in the absorption coefficients and colour parameters in Tables 5.5. Thg and Thl were more efficient than EGB. This observation was supported by the UV-visible absorption spectra for syringaldehyde treated with each mercaptan (shown in Figure 5.12a), as a decrease in absorption between 360 and 415nm (which is indicative of de-colouration) occurred with each mercaptan treatment. Furthermore, this reduction in absorption was greater for the Thg and Thl treated samples than for the EGB treated sample.



**Figure 5.12a.** The UV-visible absorption spectra for syringaldehyde treated with mercaptans.

Inhibition of reversion, as indicated by the absorption coefficients and colour parameters in Tables 5.5a-d, was again varied. EGB inhibited reversion slightly, Thg had no effect on the extent of reversion compared to the untreated sample, and Thl actually increased reversion. The UV-visible absorption difference spectra for syringaldehyde treated with mercaptans and irradiated, against respective non-irradiated samples, are shown in Figure 5.12b.





**Figure 5.12b.** The UV-visible absorption difference spectra, (as irradiated samples minus non-irradiated samples), for syringaldehyde treated with mercaptans and irradiated for 12 hours by Ultravitalux sunlamps.

In Chapter 4 it was proposed that syringaldehyde produced corresponding quinone species during irradiation. This is supported by the absorption difference spectrum for syringaldehyde upon irradiation (see Figure 5.12b), which revealed an increase in absorption at 425nm, typical of absorption by quinone species. This region, however, corresponds to a secondary absorption peak for quinones. The region of maximum absorption typically occurs at 360nm, but this region decreased upon irradiation of syringaldehyde. The absorption spectra for non-irradiated syringaldehyde (see Figure 5.12a), revealed that syringaldehyde also absorbed at 360nm. It is therefore possible that the syringaldehyde peak had masked the quinone peak in the same region. Thus, the decrease in absorption in this area during irradiation could simply have been due to a decrease in syringaldehyde species as it reacted to form other products.

Upon irradiation of syringaldehyde treated with Thg and Thl, an increase in absorption at 360nm was observed. The presence of these two species may have resulted in the formation of a new product. It is more likely, though, that their initial bleaching (see above) efficiently removed syringaldehyde species, weakening their absorption around 360nm. Therefore, the absorption maxima for quinone species formed during irradiation was no longer masked. The EGB treated sample revealed a decrease in absorption in this region upon irradiation, to a slightly lesser degree than the untreated control. The initial bleaching observed with EGB treatment of syringaldehyde was revealed to be less efficient than the bleaching by Thg and Thl (see above), so that many coniferaldehyde species may have remained in this sample after treatment. As with the untreated sample, the photo-reactions of these unreacted syringaldehyde species could then have masked the absorption by quinone products in the EGB treated sample.

An increase in absorption at 200nm, which was observed for untreated syringaldehyde upon irradiation, did not occur in any of the mercaptan treated samples, (see Figure 5.12b). All other spectral changes of the untreated sample, however, were also apparent in the mercaptan treated samples upon irradiation (excluding, of course, the 360nm peak discussed above).

It appears then, that no mercaptan was able to inhibit the photo-induced formation of quinone species for syringaldehyde. This inefficient inhibition may have been a result of reduction/oxidation cycles similar to those discussed for vanillin above (see Category 2 compounds), and shown in Figure 5.8.

### ***Summary for Category 3 compounds***

Treatment with EGB or Thg greatly inhibited photo-induced reversion in methoxyhydroquinone. This may have been a result of the initial bleaching, or removal of quinone species present in this sample, occurring via an irreversible process, thereby preventing the photo-induced reformation of these compounds. Thl did not inhibit the reversion of this MLC, nor did it bleach as efficiently, as the EGB and Thg treatments had.

Other MLCs belonging to this category were inhibited to various partial degrees by mercaptans. Inhibition was weak or nil, and in some cases reversion increased in the presence of a mercaptan. This incomplete inhibition could be attributed to photo-induced oxidation and mercaptan-induced reduction cycles being established during irradiation. A gradual depletion of the mercaptans through repeated cycles could account for the final poor inhibition. The varied inhibition observed could have resulted from different reaction rates, or different proportions of reactive intermediates produced during this cycle, as determined by the mercaptan/MLC components of the system.

### **5.3.5 Category 4 compound: Yellowing with no associated darkening**

Observations of the colour changes, and changes in the absorption coefficients and colour parameters, for acetovanillone treated with mercaptans and irradiated are shown in Tables 5.6 and 5.7. The UV-visible absorption spectra for acetovanillone treated with mercaptans are shown in Figure 5.13a, and the absorption difference spectra for these samples after irradiation are shown in Figure 5.13b.

**Table 5.6.** Observations of the colour of acetovanillone solutions treated with mercaptans and irradiated for 12 hours by Ultravitalux sunlamps.

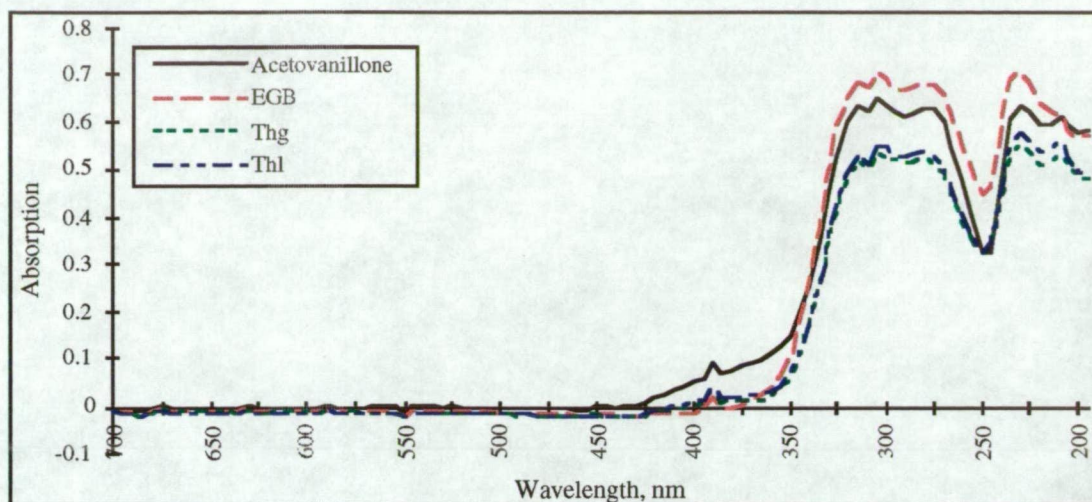
original	irradiated	mercaptan	treated	treated and irradiated
pale yellow	bright yellow	EGB	pale yellow	yellow
		Thg	yellow tinge	light yellow
		Thl	yellow tinge	yellow tinge

**Table 5.7.** Changes in the absorption coefficients,  $k$  ( $\text{g/m}^2$ )<sup>-1</sup>, and the tristimulus colour parameters,  $L^*$ ,  $a^*$  and  $b^*$ , for acetovanillone treated with mercaptans and irradiated for 12 hours by Ultravitalux sunlamps.

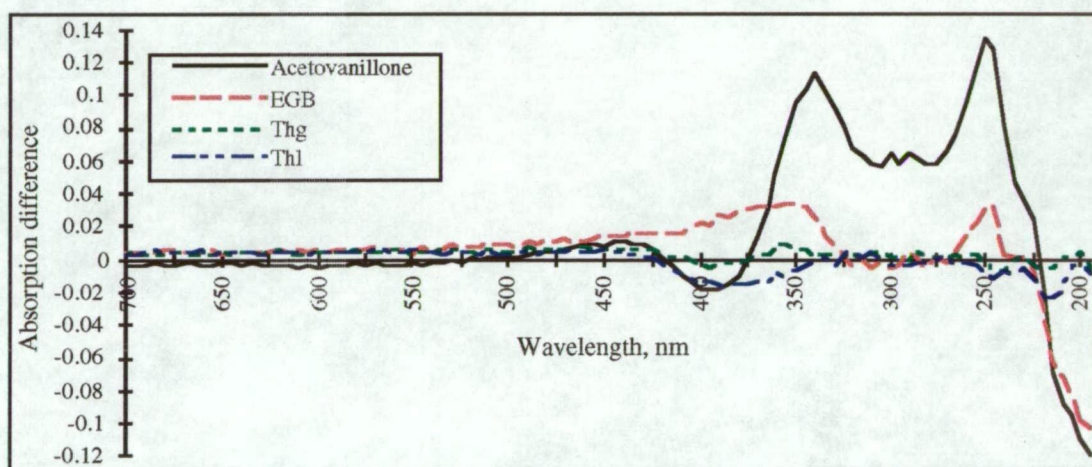
<sup>a</sup> reversion	mercaptan	<sup>b</sup> bleaching	<sup>c</sup> reversion
$\Delta k_{(12\text{hrs}-0\text{hrs})}$		$\Delta k_{(\text{treated}-\text{untreated})}$	$\Delta k_{(12\text{hrs}-0\text{hrs})}$
1.1	EGB	-1.4	0.7
	Thg	-1.7	0.4
	Thl	-1.4	0.1
$\Delta b^*_{(12\text{hrs}-0\text{hrs})}$		$\Delta b^*_{(\text{treated}-\text{untreated})}$	$\Delta b^*_{(12\text{hrs}-0\text{hrs})}$
1.5	EGB	-1.4	1.1
	Thg	-1.5	0.6
	Thl	-1.1	0.1
$\Delta L^*_{(12\text{hrs}-0\text{hrs})}$		$\Delta L^*_{(\text{treated}-\text{untreated})}$	$\Delta L^*_{(12\text{hrs}-0\text{hrs})}$
$0.06 \pm 0.03$	EGB	$0.73 \pm 0.03$	$-0.21 \pm 0.04$
	Thg	$1.03 \pm 0.03$	$-0.15 \pm 0.03$
	Thl	$0.89 \pm 0.03$	$-0.04 \pm 0.03$
$\Delta a^*_{(12\text{hrs}-0\text{hrs})}$		$\Delta a^*_{(\text{treated}-\text{untreated})}$	$\Delta a^*_{(12\text{hrs}-0\text{hrs})}$
-0.7	EGB	-0.6	0.1
	Thg	-0.7	0.0
	Thl	-0.9	0.3

Note that standard deviations are  $\pm 0.1$  unless stated otherwise. <sup>a</sup>Reversion of the untreated MLC, reviewed from Chapter 4. <sup>b</sup>Bleaching effect of mercaptans on the MLC. <sup>c</sup>Reversion of the MLC treated with mercaptans.





**Figure 5.13a.** The UV-visible absorption spectra for acetovanillone treated with mercaptans.



**Figure 5.13b.** The UV-visible absorption difference spectra, (as irradiated samples minus non-irradiated samples), for acetovanillone treated with mercaptans and irradiated for 12 hours by Ultravitalux sunlamps.

Changes in the absorption coefficients and colour parameters revealed an initial bleaching for all mercaptans, although this bleaching was incomplete as some colour still remained. This was supported by the UV-visible absorption spectra, (Figure 5.13a), as a small peak between 360 and 420nm (indicative of coloured species, or quinones) was almost completely removed by each mercaptan.

Reversion, as shown by the absorption coefficients and colour parameters, was inhibited by all three mercaptans, but to different extents. Thl inhibited completely,



Thg well, and EGB only slightly. This was supported by the UV-visible absorption difference spectra for these samples after irradiation (see Figure 5.13b). The spectra for the Thl and Thg treated samples revealed that either no significant changes, or very small changes, had occurred upon irradiation, supporting a complete, or almost complete, inhibition of photo-reversion for acetovanillone. The EGB treated sample, however, underwent changes in its absorption spectra like those of the untreated sample upon irradiation. Included in these changes was a slight re-introduction of absorption between 360 and 420nm. Thus the bleaching involving this spectral region was completely sustainable for Thg and Thl, but not for EGB treatment. It is possible that Thg and Thl may have bleached acetovanillone in an irreversible manner, thereby blocking reversion, while EGB may have bleached reversibly, such that reversion could still occur. Thg and Thl may also have reacted with acetovanillone in a similar manner as previously proposed for guaiacol, (see Category 2 compounds, Figure 5.3), resulting in a deactivation of the phenolic hydroxyl group of acetovanillone.

### 5.3.6 Category 5 compound: Small darkening but no photo-yellowing

The observations of colour changes, and changes in the absorption coefficients and colour parameters for 4-hydroxy-3-methoxy cinnamaldehyde treated with mercaptans and irradiated are shown in Tables 5.8 and 5.9. The UV-visible absorption spectra for the same compound treated with mercaptans are shown in Figure 5.14a, and the absorption difference spectra for these samples upon irradiation are shown in Figure 5.14b.

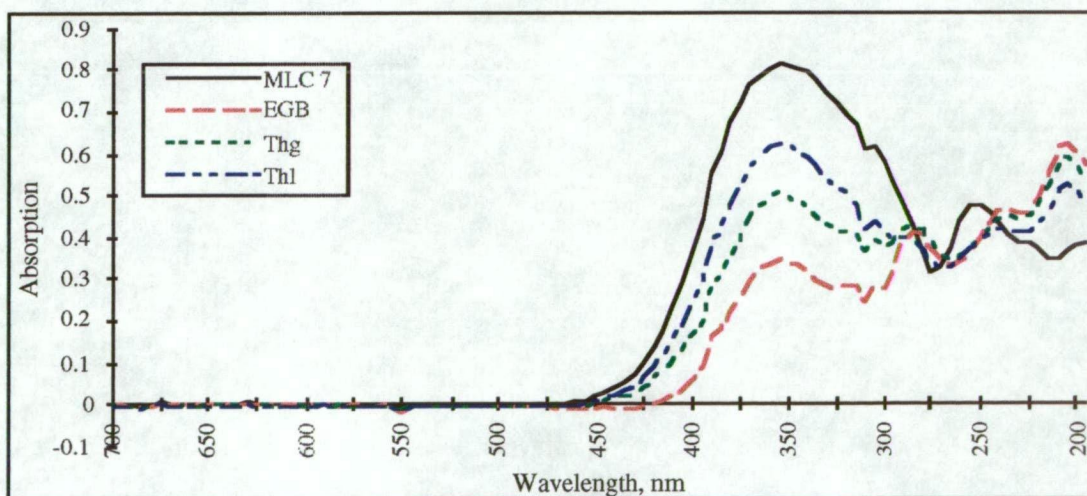
**Table 5.8.** Observations of the colour of 4-hydroxy-3-methoxy cinnamaldehyde solutions treated with mercaptans and irradiated for 12 hours by Ultravitalux sunlamps.

original	irradiated	mercaptan	treated	treated and irradiated
bright-orange	orange	EGB	light yellow	pale yellow
		Thg	light yellow	light yellow
		Thl	light yellow	yellow-orange

**Table 5.9.** Changes in the absorption coefficients,  $k$  ( $\text{g}/\text{m}^2$ )<sup>-1</sup>, and the tristimulus colour parameters,  $L^*$ ,  $a^*$  and  $b^*$ , for 4-hydroxy-3-methoxy cinnamaldehyde treated with mercaptans and irradiated for 12 hours by Ultravitalux sunlamps.

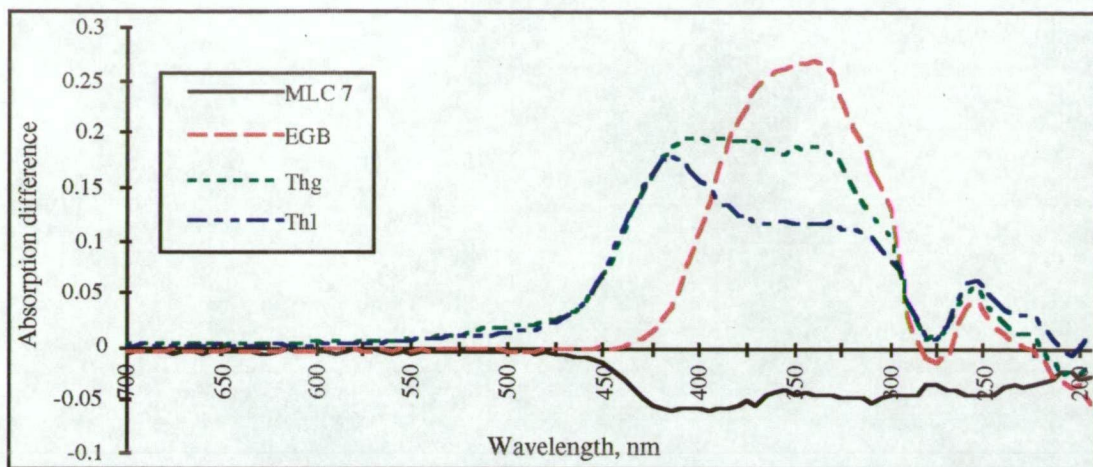
<sup>a</sup> reversion	mercaptan	<sup>b</sup> bleaching	<sup>c</sup> reversion
$\Delta k_{(12\text{hrs}-0\text{hrs})}$		$\Delta k_{(\text{treated}-\text{untreated})}$	$\Delta k_{(12\text{hrs}-0\text{hrs})}$
0.1	EGB	-2.6	0.4
	Thg	-2.3	12.2±0.3
	Thl	-1.9	13.3±0.4
$\Delta b^*_{(12\text{hrs}-0\text{hrs})}$		$\Delta b^*_{(\text{treated}-\text{untreated})}$	$\Delta b^*_{(12\text{hrs}-0\text{hrs})}$
-0.8	EGB	-4.0	0.4
	Thg	-3.3	10.8
	Thl	-2.9	12.1±0.2
$\Delta L^*_{(12\text{hrs}-0\text{hrs})}$		$\Delta L^*_{(\text{treated}-\text{untreated})}$	$\Delta L^*_{(12\text{hrs}-0\text{hrs})}$
-0.30±0.03	EGB	0.26±0.03	-0.07±0.03
	Thg	0.29±0.04	-1.33±0.04
	Thl	0.20±0.03	-1.13±0.03
$\Delta a^*_{(12\text{hrs}-0\text{hrs})}$		$\Delta a^*_{(\text{treated}-\text{untreated})}$	$\Delta a^*_{(12\text{hrs}-0\text{hrs})}$
0.9	EGB	1.5	-0.1
	Thg	1.2	-2.2
	Thl	1.0	-3.4

Note that standard deviations are  $\pm 0.1$  unless stated otherwise. <sup>a</sup>Reversion of the untreated MLC, reviewed from Chapter 4. <sup>b</sup>Bleaching effect of mercaptans on the MLC. <sup>c</sup>Reversion of the MLC treated with mercaptans.



**Figure 5.14a.** The UV-visible absorption spectra for 4-hydroxy-3-methoxy cinnamaldehyde treated with mercaptans.





**Figure 5.14b.** The UV-visible absorption difference spectra, (as irradiated samples minus non-irradiated samples), for 4-hydroxy-3-methoxy cinnamaldehyde treated with mercaptans and irradiated for 12 hours by Ultravitalux sunlamps.

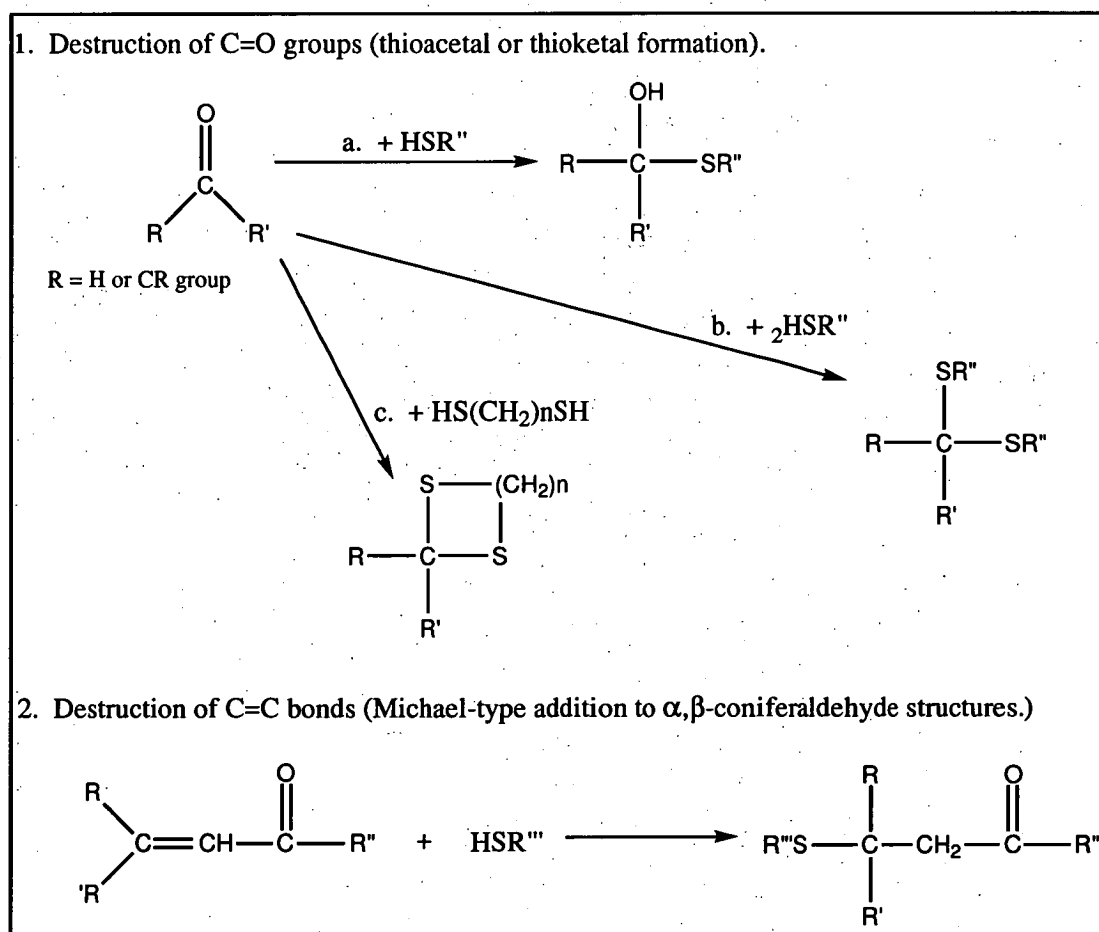
Changes in the absorption coefficients and colour parameters in Table 5.9 showed that bleaching had occurred upon treatment with all the mercaptans, with the efficiency of EGB being greater than Thg, which in turn was greater than the efficiency of Thl. The UV-visible absorption spectra in Figure 5.14a revealed that each mercaptan treatment had resulted in several increases in absorption below 300nm. This is likely to be simply due to the mercaptans' presence, however, as this region coincides with that of absorption observed for mercaptans alone (see Figure 5.1).

The large peak at 360nm was reduced by each mercaptan treatment, with order of magnitude complying to the order of the bleaching efficiency revealed by the absorption coefficients and colour parameters. This removal of absorption at 360nm supports the proposal in Chapter 3 that the bleaching action of mercaptans on TMP handsheets involves the removal of coniferaldehyde structures (see Figures 3.5 and 3.6). For the EGB treated sample, absorption ceased at 415nm, while for Thg and Thl absorption ceased at 450-460nm as with the untreated sample.

Despite the initial interactions and bleaching just described, no inhibition of photo-induced reversion was observed by the absorption coefficients or colour parameters. In fact, all three mercaptans had increased reversion, EGB to a small degree only, but Thg and Thl drastically. This was supported by changes in the UV-visible absorption difference spectra for the mercaptan-treated samples upon irradiation (see Figure 5.14b). This spectra revealed that 4-hydroxy-3-methoxy cinnamaldehyde underwent no formation of coloured products on its own, as there was no increase in absorption across the whole spectrum. In fact, a small decrease in absorption across the whole range for this MLC indicates that photo-bleaching may have occurred. In

the presence of each mercaptan, however, large increases in absorption were observed. For EGB, this absorption increase occurred as one large peak centred at 360nm. This suggests that irradiation had caused a re-formation of the original MLC. This may also have been the case for the Thg and Thl treated samples, but this region had been overlapped by two other large absorption peaks, formed on irradiation of these samples. That is, irradiation of the Thg and Thl treated samples resulted in large increases in absorption between 310 and 355nm, and between 380 and 470nm, tailing to about 550nm. These regions are typical for irradiated quinone species. This would explain the greater discolouration for the Thg and Thl treated samples over the EGB treated sample, as quinones are more strongly coloured than cinnamaldehyde.

It has been suggested that mercaptans bleach coniferaldehyde species via Michael-type addition reactions onto the side chain C=C bond<sup>97,101</sup>, thereby destroying the conjugation responsible for colour. Alternatively, they may destroy carbonyl groups via thioacetal formation<sup>101</sup>. These reactions are shown in Figure 5.15.



**Figure 5.15.** Possible reactions of thiols with aldehyde / coniferaldehyde structures<sup>97,101</sup>.

In the case of both of the reactions presented in Figure 5.15, conjugation between the  $C_{\alpha}=C_{\beta}$  and  $C=O$  group is destroyed. This would account for the initial bleaching that was observed. In Chapter 4, it was revealed that MLCs containing this kind of conjugation failed to photo-revert. It was proposed that the  $C=O$  group may have interfered with sensitisation of the  $C=C$  group, thereby preventing photo-yellowing reactions from occurring. It is therefore possible that the bleaching of coniferaldehyde species with mercaptans, by destroying the side chain conjugation, may actually have been responsible for its subsequent photo-yellowing.

Therefore, although the results for this MLC supports the bleaching action of mercaptans on TMP as removal of coniferaldehyde species (proposed in Chapter 3), it does not seem likely that this bleaching action was responsible for the inhibition of reversion seen in Chapter 3 for TMP treated with mercaptans.

## 5.4 Conclusions

### The behaviour of mercaptans upon irradiation

- Mercaptans were found to dimerise during irradiation. This dimerisation may involve hydrogen abstraction at their SH groups, creating thiol radicals. These could then combine to form dimers across disulphide bonds. The abstracted hydrogen could be donated to radical intermediates of photo-yellowing reactions, thus inhibiting the formation of yellow products.
- For EGB in particular, photo-reactions or dimerisation may involve an initial UV-absorption and sensitisation at its  $C=O$  groups. This represents a further mechanism by which these compounds may inhibit reversion, i.e. by behaving as UV-absorbers or shielding a chromophoric group from UV radiation.

### Inhibition of the reversion of various MLCs by mercaptans

Three distinct inhibitory responses were observed for a range of MLCs treated with mercaptans and irradiated. These were:

a) a complete inhibition of reversion by all mercaptan treatments (guaiacol, isoeugenol and vanillic acid);

b) a partial inhibition, no inhibition or enhanced discolouration by all mercaptan treatments (quinone species, vanillin and syringaldehyde); and

c) an introduction of photo-induced yellowing by treatment with each mercaptan (3-methoxy-4-hydroxy cinnamaldehyde).

It appeared that each of these responses may have involved different "inhibitory" mechanisms. These are discussed below:

*a) Complete inhibition observed by each mercaptan (guaiacol, isoeugenol, and vanillic acid)*

- Each of these MLCs were 3-methoxy-4-hydroxy compounds which contained either no further substitution (guaiacol), or substitution at the C1 position of a COOH group (vanillic acid) or a 3-carbon side chain (isoeugenol).
- For these compounds it appeared that Thg and Thl may have imparted similar mechanisms of inhibition, which were different to those of EGB.
- Thg and Thl may have inhibited reversion via an initial reaction with the MLC which arrested reversion at an early stage. This may have involved a removal of the phenolic hydroxyl group of the MLC, (which was shown in Chapter 4 to be essential for photo-reversion to occur), via reaction with the COOH group of these thiocarboxylic acids.
- For EGB, no initial reaction with these MLCs was indicated. This suggested that EGB inhibition may have occurred as ongoing processes during irradiation (for example, by shielding MLCs from UV radiation, by removing coloured species as they were formed, or by behaving as a hydrogen donor or radical scavenger during irradiation).

*b) Partial inhibition, no inhibition, or an increase in reversion observed by mercaptans (quinone species, vanillin, and syringaldehyde)*

- 3-methoxy-4-hydroxy compounds which contained a phenolic or aldehyde group substituted at the C1 position responded with partial or no inhibition, or even an increase in reversion upon treatment with mercaptans.
- Except for methylhydroquinone, which was originally colourless, an initial bleaching of these MLCs was observed for each mercaptan treatment.

- As inhibition for methoxyhydroquinone was almost complete by EGB and Thg treatments, the initial bleaching by these mercaptans may have occurred via an irreversible process, preventing the re-formation of coloured quinone species. This was not the case for Thl.
- Alternatively, for methoxyhydroquinone and vanillin the initial bleaching by thiols may have involved a reduction of quinone species (which were originally present in both these MLC samples, as a result of atmospheric oxidation), or a Michael-type addition of the thiols to these quinones, resulting in the formation of a corresponding *p*-hydroquinone compound that either contained or did not contain a thiol residue.
- This hydroquinone species could then have undergone photo-oxidation during irradiation, to re-form its corresponding quinone. Subsequent reduction of this quinone species by mercaptans would establish a reduction-oxidation-reduction cycle. As this cycle proceeds, a gradual depletion of active thiol groups would result in an overall inefficiency in inhibition.
- Inhibition of reversion by each mercaptan may have occurred via this mechanism even if the initial bleaching had not occurred. In such a case, the cycle would be initiated by mercaptan-induced reduction of quinones produced during photo-reversion.
- The varied efficiencies of inhibition observed for the MLCs treated with each mercaptan could be a result of differing rates of the reactions involved in the above cycle, with each reaction rate being dependent on different MLC-mercaptan components of each system.

*c) An introduction of reversion by each mercaptan (3-methoxy-4-hydroxy cinnamaldehyde).*

- For 3-methoxy-4-hydroxy cinnamaldehyde, reversion was introduced by each mercaptan. It is possible that the initial bleaching reaction of mercaptans on this MLC was responsible for its subsequent reversion, by destroying the side chain conjugation of this MLC. In Chapter 4 it was suggested that it was this conjugation which had prevented this MLC from photo-yellowing in the first place.
- The presence of Thg and Thl may also have resulted in the formation of coloured quinone species during irradiation of this MLC, resulting in an enhanced discolouration.



*d) Exceptions (eugenol and acetovanillone)*

- Eugenol appeared to have undergone initial interactions with each mercaptan which were similar to those observed for compounds that underwent complete inhibition (e.g. guaiacol). Eugenol, however, experienced no inhibition by any mercaptan.
- It is possible that reaction rates for interactions between eugenol and the thiocarboxylic acid mercaptans may have been too slow for effective inhibition to occur.
- Alternatively, it is possible that the presence of an end group C=C bond on the 3-carbon side chain of this MLC could have altered its reactions, or at least reaction rates, with the mercaptans.
- Thg-eugenol and Thl-eugenol complexes, formed by reactions of eugenol with these two mercaptans, may also have photo-sensitised or otherwise enhanced yellowing reactions of this MLC that were normally minor.
- Acetovanillone responded with a varied bleaching and inhibition upon treatment with each mercaptan. Thl completely inhibited, Thg inhibited well, and EGB inhibited only partially. The results for this compound were very similar to those discussed in point b above. Unlike the compounds discussed above, however, acetovanillone did not contain a phenolic hydroxyl or aldehyde group at the C1 position.

Therefore, the inhibition of reversion by mercaptans appears to be diverse and complex. It seems that several different mechanisms occur, which are dependent on both the type of mercaptan used, and the type of compound it is acting on. Three possible mechanisms for the inhibition that has been observed will be investigated in Chapter 6.

## CHAPTER 6

# AN INVESTIGATION INTO SEVERAL MECHANISMS BY WHICH MERCAPTANS MAY INHIBIT REVERSION

In Chapter 5, various inhibition effects were revealed for EGB, Thg and Thl acting on the reversion of a range of MLCs. The diversity in these results suggests that mercaptans may exhibit several different methods of inhibition, which vary according to both the mercaptan used and the compound it is acting on. In this chapter three possible mechanisms for inhibition of reversion by mercaptans will be explored. These are as follows:

1. A "removal" mechanism, which will be tested for both TMP and BTMP handsheets, and for various MLCs. This mechanism involves the mercaptans removing coloured products as they are formed. For example, they may remove coloured quinone species produced during irradiation, by reducing them or adding to them via Michael-type addition reactions. This mechanism will be discussed in Section 6.1.
2. An inhibition of sensitisation reactions during reversion. This mechanism involves the mercaptans blocking, or otherwise deactivating, photo-sensitised reversion processes. Photo-sensitised reversion is a reversion response which has been enhanced by the presence of a secondary, photo-excitabile, compound or functional group. These compounds often contain carbonyl groups which can absorb UV radiation, after which they are transformed into a high-energy (or excited) state. While in this state they are then able to activate photo-reversion of other compounds, either causing an enhanced discolouration or, in cases where photo-yellowing is not normally observed by a compound, they may even induce photo-yellowing reactions. As these compounds do not usually undergo photo-yellowing themselves, they are referred to as photo-sensitisers. The possibility that mercaptans may inhibit reversion by interfering with the activity of these photo-sensitisers will be explored in Section 6.2.
3. A UV absorption or "shielding" mechanism. This mechanism involves the mercaptans absorbing UV radiation, thereby shielding a photo-reactive compound. For example, EGB may absorb UV radiation at its carbonyl groups (prior to abstraction of its thiol-hydrogen atom and subsequent dimerisation, see Chapter 5). After absorbing this radiation, the EGB may then release it as non-harmful thermal energy, thereby effectively shielding other chromophoric groups from UV radiation. This mechanism is discussed in Section 6.3.

## **6.1 “Removal Mechanism”: Removal of Coloured Species as they are Formed**

### **6.1.1 Introduction**

In Chapter 1, Section 1.3, several hypothetical mechanisms for inhibition of reversion by mercaptans were presented. One of these mechanisms, first suggested by Cole and Sarkanen<sup>97</sup>, involved a retardation of photo-yellowing by eliminating coloured species as they were formed. For example, quinones formed during irradiation may be removed by mercaptans via reduction or Michael-type addition of the thiol groups to the quinones<sup>97</sup>. This is not considered a “true” inhibition, as the products of yellowing are still formed.

Results presented in Chapter 5 revealed this to be a possible mechanism for the inhibition of reversion of several MLCs, (particularly quinone species and 3-methoxy-4-hydroxy compounds with an aldehyde substitution at the C1 position, e.g. vanillin). An example of such a mechanism was shown in Figures 5.7 and 5.8.

One method of testing the ability of mercaptans to act via this mechanism is simply to see if the mercaptans are able to bleach pre-irradiated handsheets (or MLC compounds) back to their original brightness<sup>97</sup>. If this is achieved, then the mercaptans have the ability to remove the photo-induced yellow species completely, and therefore could possibly act by removing them as they are formed during irradiation. Note that a complete recovery to the original brightness does not necessarily prove a complete inhibition via this process, however. Removal of native chromophores pre-existent in the handsheet may occur concurrently with removal of those produced by irradiation, further contributing to a reduced colouration. The test is therefore a measure of the *potential* of a “removal mechanism”, rather than an accurate measure of its actual existence.

In this section, the ability of EGB to bleach pre-exposed TMP and BTMP handsheets are presented, as EGB was found to be the most favourable inhibitor for these lignin-rich handsheets in Chapter 3.

Following this is a more in-depth study of the ability of mercaptans to bleach pre-exposed model lignin compounds back to their original state. The three mercaptans discussed in the previous chapters were tested, due to their varying efficiencies in inhibiting the reversion of model lignin compounds found in Chapter 5. All model compounds which had undergone photo-reversion in Chapter 4 were tested for the ability of each mercaptan to remove the yellow products of irradiation. The study

was not limited to compounds that had only experienced a complete inhibition by treatment with a mercaptan, as the *potential* for such a mechanism was also sought. For example, if a mercaptan was successful in completely removing coloured products of irradiation, despite a previously shown inability to inhibit their production, then the *potential* for a “removal” mechanism could be assumed, with some competition during irradiation favouring yellowing reactions. The MLCs will be discussed in separate groups, depending on their inhibition responses previously observed in Chapter 5.

### 6.1.2 Specific Methods

#### Handsheet tests

Duplicate TMP and BTMP handsheets were prepared and irradiated for 5 hours as previously described in Chapter 3. The irradiated handsheets were soaked in 5% solutions of ethylene glycol bithioglycolate in acetone for 5 minutes and then dried. The absorption coefficients,  $k$ , were then measured for and derived as previously described in Chapter 3. Solvent (acetone) controls were also included. The amount of chemical incorporated into the handsheet (% load) was determined by calculating the percent changes in weight before and after treatments.

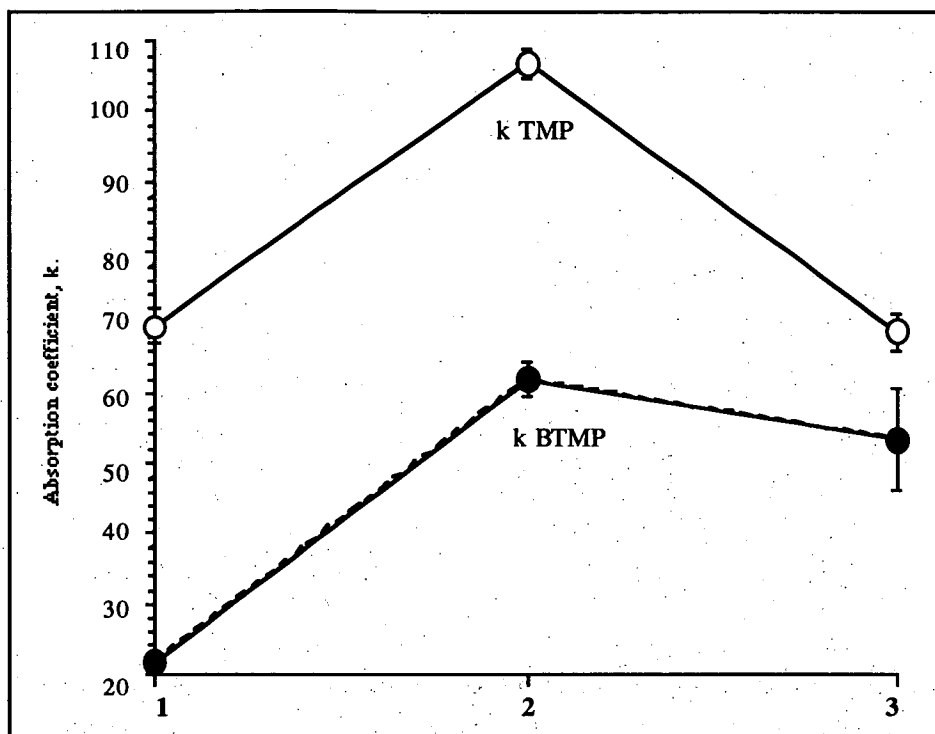
#### Model lignin compounds

0.5% solutions of each MLC in DMF were irradiated for 12 hours, as previously described in Chapter 4. One drop of the mercaptan was added to a Pasteur pipette load of the irradiated MLC solution in a small glass vial, which had been wrapped in aluminium foil to minimise light interference. The solutions were left overnight to react. They were then adsorbed onto filter paper and measured following the same procedures described in Chapter 4.

### 6.1.3 Results and Discussion

#### Handsheet tests

Figure 6.1 shows the absorption coefficients for TMP and BTMP handsheets both prior to and after irradiation, and after subsequent treatment of the irradiated samples with EGB. The solvent controls, which were treated with acetone alone, did not deviate from the untreated controls so are not presented in this figure.



**Figure 6.1.** The absorption coefficients,  $k$  ( $\text{g/m}^2$ )<sup>-1</sup>, for TMP and BTMP handsheets: 1 = original value; 2 = after 5 hours of irradiation by Ultravitalux sunlamps; 3 = after addition of EGB to irradiated samples.

It is clear from this figure that for irradiated TMP the absorption coefficient was restored to its original value by the addition of EGB. Therefore, the number of chromophores absorbing at 457nm in this handsheet (which is proportional to  $k_{457}$ , see Section 1.4), had been reduced to the original state. That is, EGB was able to completely (or at least partially, depending on the extent of concurrent “native” chromophore removal, see Section 6.1.1) remove the yellow species absorbing at this wavelength that had been formed during irradiation. This indicates that the inhibition of reversion of TMP by EGB treatment, previously shown to occur in Chapter 3, could have occurred via a removal of coloured species as they were formed.

For BTMP (which had also experienced inhibition of reversion following treatment with EGB in Chapter 3), the absorption coefficient was reduced only slightly after EGB treatment of the irradiated sample (see Figure 6.1). The reduction in the number of chromophores was therefore minimal, with the original state not even approached. Thus a “removal mechanism” either does not occur, or occurs only to a small degree, for BTMP treated with EGB and irradiated. It appears then, that other mechanisms of inhibition were responsible for the inhibited reversion of BTMP by treatment with EGB, shown in Chapter 3.

It is possible that for both TMP and BTMP, a combination of reversion inhibiting pathways occur simultaneously, with different pathways dominating, depending on the different pulp treatments.

### Model lignin compounds:

#### *a. Compounds which had experienced a complete, or almost complete, inhibition of reversion by each mercaptan treatment in Chapter 5*

**Brief history:** Guaiacol, isoeugenol and vanillic acid experienced a complete, or almost complete, inhibition of reversion by each mercaptan treatment in Chapter 5. It was suspected from the results presented in Chapter 5, that Thg and Thl had inhibition reversion of these compounds in similar ways, which were different to the action of EGB. It was suggested that the inhibition by Thg and Thl may have involved an initial reaction which prevented reversion from proceeding, whereas EGB may have acted via ongoing processes during irradiation, for example by removing coloured species as they were formed.

Observations of the colour changes in guaiacol, isoeugenol and vanillic acid resulting from irradiation and subsequent treatment with each mercaptan are shown in Table 6.1.

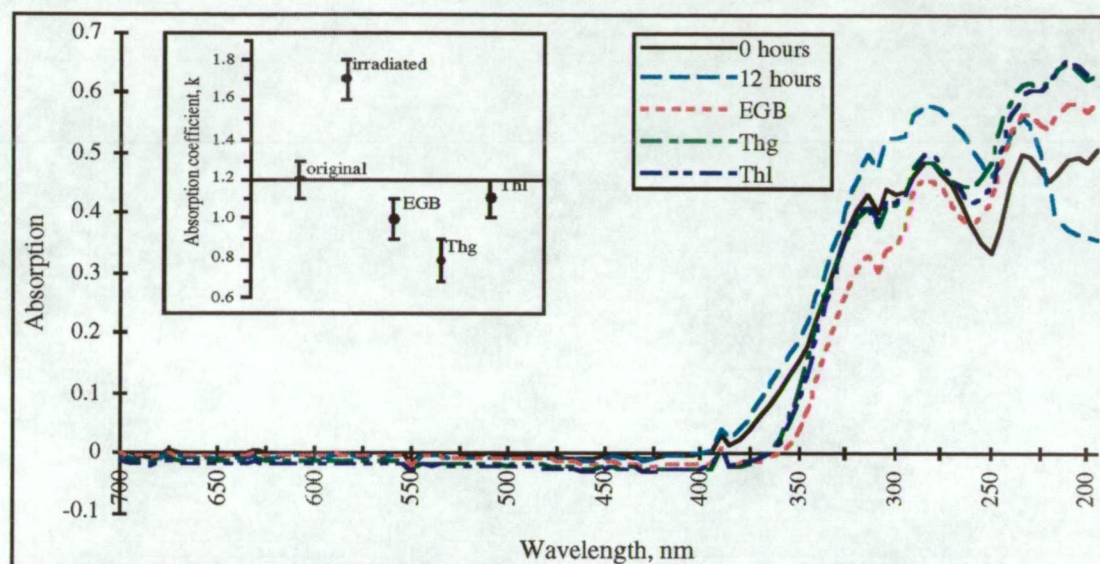
**Table 6.1.** Observations of the colour changes in guaiacol, isoeugenol and vanillic acid resulting from irradiation and subsequent treatment of the irradiated samples with each mercaptan.

MLC, and its original colour	Colour of MLC after 12 hrs of irradiation	Mercaptan treatment	Colour of irradiated MLC after treatment
Guaiacol: colourless	pale orange	EGB	paler orange
		Thg	orange tinge
		Thl	paler orange
Isoeugenol: colourless	orange tinge	EGB, Thg & Thl	colourless
Vanillic acid: colourless	light orange-yellow	EGB & Thg	pale orange-yellow
		Thl	paler orange yellow

From the observations presented in Table 6.1, it appears that irradiated isoeugenol was returned to its original colourless state after treatment with each mercaptan. Irradiated guaiacol and vanillic acid had both been bleached by each mercaptan, but not back to their original state. These observations are discussed further below, along with the absorption coefficients and UV-visible absorption spectra for each sample.



The absorption coefficients,  $k$ , and UV-visible absorption spectra for isoeugenol before irradiation, after irradiation, and after subsequent treatment of the irradiated samples with the three mercaptans are presented in Figure 6.2.



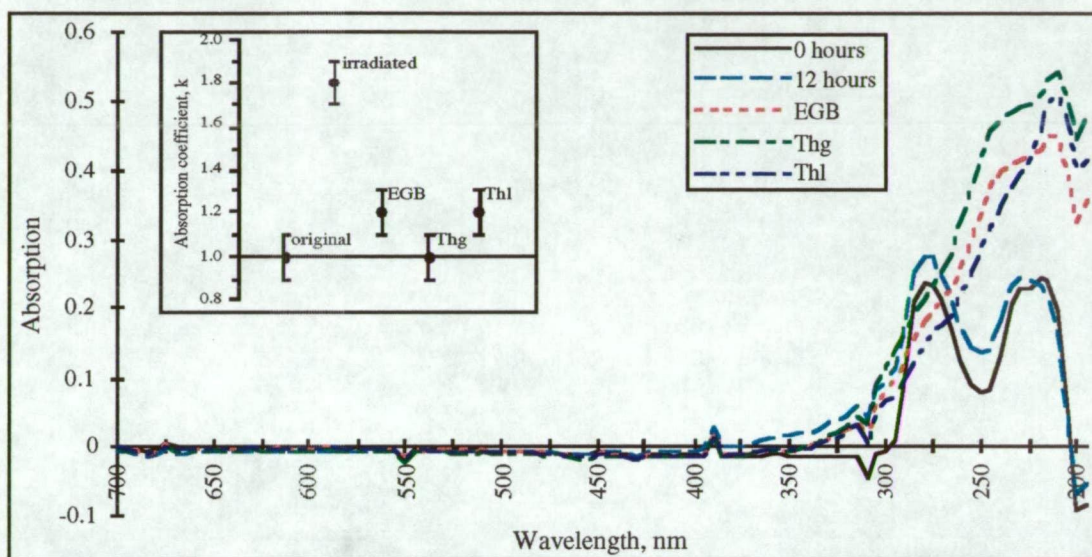
**Figure 6.2.** The absorption coefficients,  $k$  ( $\text{g}/\text{m}^2$ )<sup>-1</sup>, and UV-visible absorption spectra for isoeugenol prior to and after 12 hours of irradiation by Ultravitalux sunlamps, and after treatment of the irradiated samples with EGB, Thg and Thl.

The absorption coefficients confirmed the observations presented in Table 6.1, that all mercaptans were able to remove the photo-induced chromophoric products of isoeugenol to the original state. In fact, particularly for Thg and EGB, the chromophore content was even reduced to less than the original. The UV-visible absorption spectra also support this observation, as each mercaptan treatment had removed all absorption beyond 350nm, (which was likely to be due to coloured species present in the irradiated sample), to less than the original. Therefore, each mercaptan contains the ability to completely remove the yellow products of irradiated isoeugenol as they are formed.

Note that these results do not prove that mercaptans inhibited the reversion of isoeugenol by removing coloured species as they were formed during irradiation. Radiation may alter such a mechanism, or enhance other inhibitory actions. What these results do prove is that the mercaptans have the *ability* to impart this kind of mechanism, so potentially they *may have* inhibited the photo-reversion of isoeugenol via a “removal” mechanism.



The absorption coefficients,  $k$ , and UV-visible absorption spectra for guaiacol before irradiation, after irradiation, and after subsequent treatment of the irradiated samples with the three mercaptans are presented in Figure 6.3.



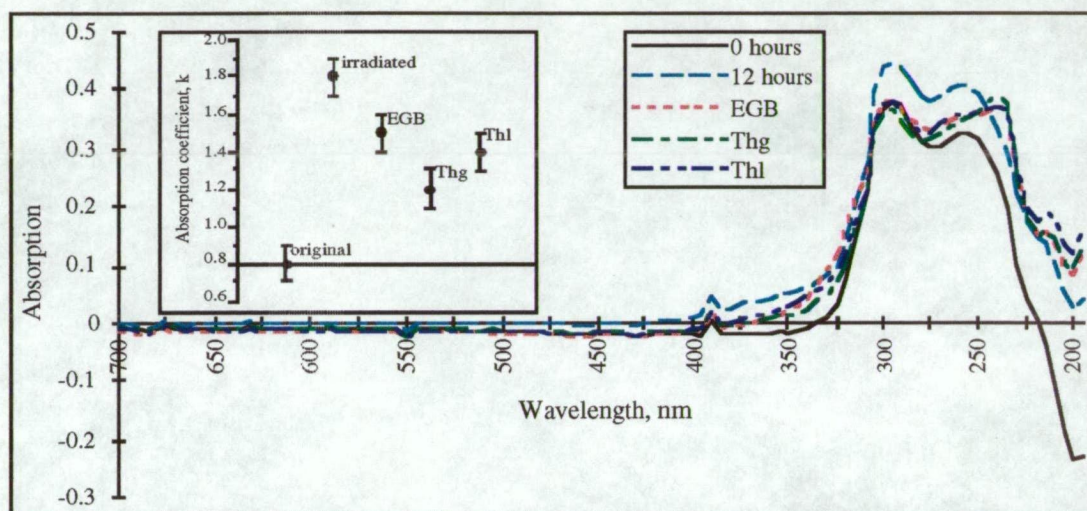
**Figure 6.3.** The absorption coefficients,  $k$  ( $\text{g/m}^2$ )<sup>-1</sup>, and UV-visible absorption spectra for guaiacol prior to and after 12 hours of irradiation by Ultravitalux sunlamps, and after treatment of the irradiated samples with EGB, Thg and Thl.

Although the absorption coefficient,  $k$ , appeared to have been reduced to its original state (within error) after treating irradiated guaiacol with Thg (see Figure 6.3), the UV-visible absorption spectra revealed that Thg had only partially removed coloured species which had been produced during irradiation. That is, the absorption peak produced at 300-420nm by irradiation of guaiacol, (which can be attributed to the formation of coloured species, possibly quinones, see Chapter 4, Section 4.3.3), was reduced by treatment with Thg, but not removed. This same peak was also reduced by treatments with EGB and Thl, as were the absorption coefficients. Therefore, each mercaptan contains the ability to remove coloured species as they are formed in guaiacol, but not completely. This mechanism would therefore be unlikely to result in a complete inhibition. As complete inhibition of reversion by each mercaptan acting on guaiacol was shown in Chapter 5, it follows that other mechanisms of inhibition had also occurred for this MLC, possibly in conjunction with a “removal” mechanism.



## Vanillic acid

The absorption coefficients,  $k$ , and UV-visible absorption spectra for vanillic acid before irradiation, after irradiation, and after subsequent treatment of the irradiated samples with the three mercaptans are presented in Figure 6.4.



**Figure 6.4.** The absorption coefficients,  $k$  ( $\text{g/m}^2$ )<sup>-1</sup>, and UV-visible absorption spectra for vanillic acid prior to and after 12 hours of irradiation by Ultravitalux sunlamps, and after treatment of the irradiated samples with EGB, Thg and Thl.

The reduction in the absorption coefficient, and therefore chromophore content, which was observed upon treatment of irradiated vanillic acid with each mercaptan (see Figure 6.4), did not come close to the original value. A broad peak at 350nm in the UV-visible absorption spectra for irradiated vanillic acid (which was introduced upon irradiation by the formation of coloured species, possibly quinones, see Chapter 4, Section 4.3.3) was also reduced by each mercaptan, but not completely removed. These results suggest that each mercaptan contains the ability to remove coloured products of irradiation of vanillic acid as they are formed, but only to a small degree. As complete inhibition was previously observed in Chapter 5 for this compound treated with each mercaptan, a “removal” mechanism was only likely to have played a minor role in the observed inhibition, with alternate inhibitory processes being dominant.

### *In summary*

Each mercaptan contains the ability to remove coloured species as they are formed during the irradiation of each MLC discussed above. The efficiency of this ability differs, however, depending on the MLC each mercaptan is acting on. While each mercaptan has the potential to effect a complete inhibition on the reversion of

isoeugenol, they are only able to effect a partial inhibition on guaiacol, and a poor inhibition on vanillic acid via this mechanism. As each of these MLCs had been shown to have undergone a complete inhibition of reversion by each mercaptan in Chapter 5, other inhibitory processes must also have been active, at least for guaiacol and vanillic acid.

***b. Compounds which experienced a partial inhibition, no inhibition, or increased reversion, after treatment with each mercaptan in Chapter 5***

**Brief history:** Compounds which experienced a partial inhibition, no inhibition, or an increase in reversion by each mercaptan treatment in Chapter 5 were acetovanillone, eugenol, syringaldehyde, vanillin, and the quinone species. It was proposed in Chapter 5 that, for each mercaptan, a "removal" mechanism (involving the removal of quinone photo-oxidation products) may have played a major role in the inhibition of these compounds, at least for vanillin, syringaldehyde and the quinone species. An overall inefficiency due to competing yellowing reactions was suspected.

Observations of the colour changes in acetovanillone, eugenol, syringaldehyde and vanillin resulting from irradiation and subsequent treatment with each mercaptan are shown in Table 6.2. The quinone species will be discussed separately.

**Table 6.2.** Observations of the colour changes in acetovanillone, eugenol, syringaldehyde, and vanillin resulting from irradiation and subsequent treatment with each mercaptan.

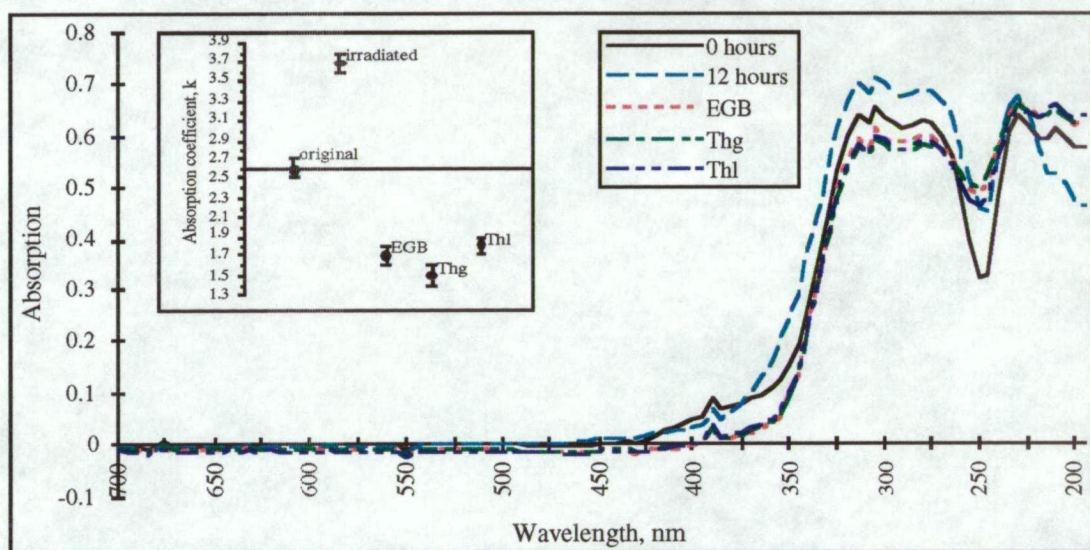
MLC, and its original colour	Colour of MLC after 12 hrs of irradiation	Mercaptan treatment	Colour of irradiated MLC after treatment
Acetovanillone: pale yellow	bright yellow	EGB & Thl	light orange-yellow
		Thg	light yellow
Eugenol: colourless	pale yellow	EGB, Thg & Thl	almost colourless
Syringaldehyde: yellow tinge	light orange-yellow	EGB & Thl	lighter orange-yellow
		Thg	pale orange-yellow
Vanillin: colourless	light orange	EGB	lighter orange
		Thg	orange-yellow
		Thl	darker orange-yellow



From this table it appears that no mercaptan was able to restore any of these irradiated MLCs back to their original colour. This will be discussed further below, along with changes in the absorption coefficients and UV-visible absorption spectra by treatment of each irradiated MLC with the mercaptans.

### Acetovanillone

The absorption coefficients,  $k$ , and UV-visible absorption spectra for acetovanillone before irradiation, after irradiation, and after subsequent treatment of the irradiated samples with the three mercaptans are presented in Figure 6.5.



**Figure 6.5.** The absorption coefficients,  $k$  ( $\text{g/m}^2$ )<sup>-1</sup>, and UV-visible absorption spectra for acetovanillone prior to and after 12 hours of irradiation by Ultravitalux sunlamps, and after treatment of the irradiated samples with EGB, Thg and Thl.

All the mercaptans tested removed the chromophore content of the irradiated sample to below the original level, as revealed by the reduction in the absorption coefficient in Figure 6.5. The UV-visible absorption spectra revealed a reduction in absorption beyond 350nm to below that of the original, non-irradiated sample. This is a further indication of the removal of coloured species to below the original level. Therefore, each mercaptan appears to have also bleached unreacted acetovanillone which may have remained in the sample as well as removing the coloured products formed by irradiation of acetovanillone. At any rate, it is clear from these results that each mercaptan contains the ability to completely remove the coloured products of irradiated acetovanillone as they are formed.

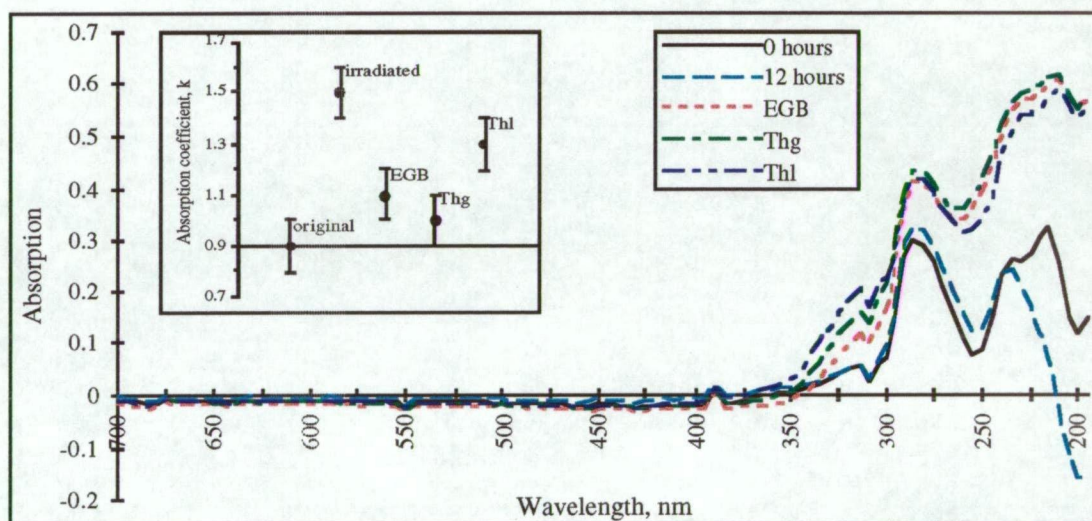
In Chapter 5, however, it was revealed that only Thl had completely inhibited the reversion of acetovanillone. Thus, for Thl it is possible that it had acted via



removing coloured species as they were formed. For Thg, an almost complete inhibition of reversion was found in Chapter 5, so a removal mechanism could also have been effective for Thg in this case, but at a slightly slower rate such that some of the products of competing photo-yellowing reactions were still apparent. EGB had only effected a slight inhibition of reversion of acetovanillone in Chapter 5, so while the potential for a “removal” mechanism existed, it was certainly not effective for EGB acting on acetovanillone during irradiation. Perhaps it occurred, but at such a slow rate that only a few products of photo-yellowing were removed.

### Eugenol

The absorption coefficients,  $k$ , and UV-visible absorption spectra for eugenol before irradiation, after irradiation, and after subsequent treatment of the irradiated samples with the three mercaptans are presented in Figure 6.6.



**Figure 6.6.** The absorption coefficients,  $k$  ( $\text{g}/\text{m}^2$ )<sup>-1</sup>, and UV-visible absorption spectra for eugenol prior to and after 12 hours of irradiation by Ultravitalux sunlamps, and after treatment of the irradiated samples with EGB, Thg and Thl.

Treatment of irradiated eugenol with each mercaptan resulted in a reduction in the absorption coefficient, and therefore chromophore content, but not to the state of the original non-irradiated sample (see Figure 6.6). This was also observed in Table 6.2, as the pale yellow irradiated MLC solution was returned almost to its original colourless state by each mercaptan treatment. Therefore, each mercaptan contains the potential to remove chromophoric products of irradiation of eugenol as they are formed, but not to a large extent. In Chapter 5 it was revealed that no mercaptan was able to inhibit, even partially, the photo-reversion of eugenol. Therefore, even if the mercaptans did remove some chromophoric products in eugenol during irradiation,

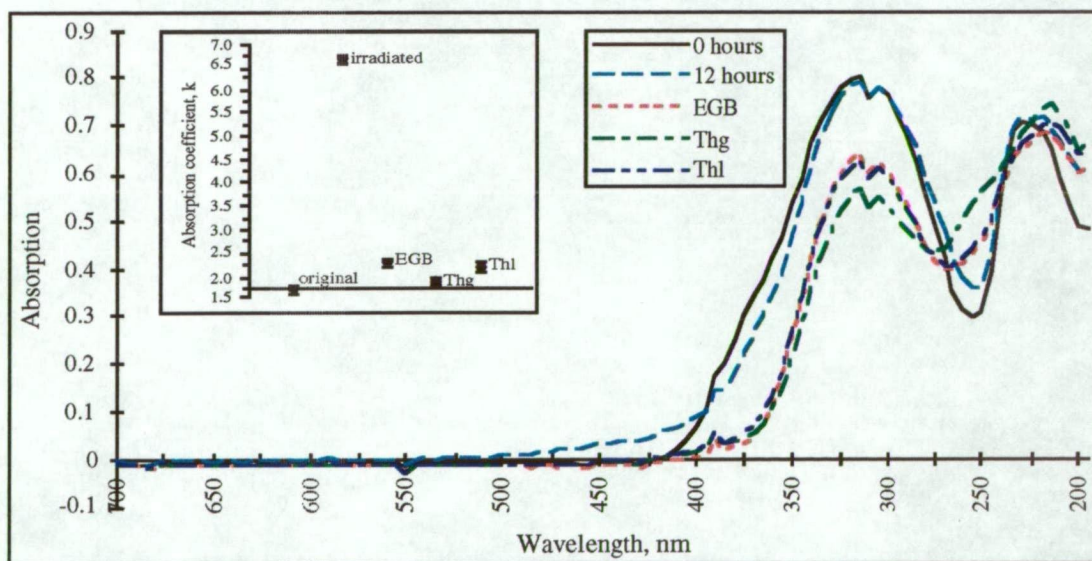


the effect was very weak and was overwhelmed by competing photo-yellowing reactions.

The UV-visible absorption spectra for irradiated eugenol treated with each mercaptan (see Figure 6.6) did not support the observations discussed above, as no mercaptan treatment had resulted in any reduction in absorption that would be indicative of colour removal (i.e. there was no reduction in absorption above approximately 350nm). In fact, an increase in absorption can be seen in this figure at 320nm for each mercaptan treatment. For Thg and Thl, an increase in absorption at 320nm was also observed when they were applied to non-irradiated eugenol in Chapter 5 (see Figure 5.9a). The peak in Figure 6.6 in this region could therefore represent a reaction product of residual (i.e. non-irradiated) eugenol with Thg or Thl. For EGB, absorption in this region did not increase after treatment of the non-irradiated MLC in Chapter 5, but it had increased significantly after irradiation of this EGB treated sample, (see Figures 5.9a and b). So, the increase in absorption, observed at 320nm upon treatment of irradiated eugenol with EGB in Figure 6.6, could represent a reaction product of irradiated eugenol (or a product of irradiated eugenol) with EGB.

### *Syringaldehyde*

The absorption coefficients,  $k$ , and UV-visible absorption spectra for syringaldehyde before irradiation, after irradiation, and after subsequent treatment of the irradiated samples with the three mercaptans are presented in Figure 6.7.



**Figure 6.7.** The absorption coefficient,  $k$  ( $\text{g/m}^2$ )<sup>-1</sup>, and UV-visible absorption spectra for syringaldehyde prior to and after 12 hours of irradiation by Ultravitalux sunlamps, and after treatment of the irradiated samples with EGB, Thg and Thl.

Each mercaptan tested removed the photo-induced chromophoric species of irradiated syringaldehyde back to almost the original state, as shown by the reductions in the absorption coefficients in Figure 6.7. The UV-visible absorption spectra concurred with this, as a broad absorption peak centred around 420nm for the irradiated sample (which was attributed to the formation of yellow products of irradiation, probably quinone species, in Chapter 4), was completely removed by each mercaptan treatment. A shoulder at 360nm also appears to have been removed by each mercaptan, although this region has a large overlap with the absorption for syringaldehyde itself, so is difficult to distinguish. These two regions represent primary (360nm) and secondary (425nm) absorption maxima for quinone species, so it is therefore possible that the mercaptans are able to remove quinone species as they are formed during the irradiation of syringaldehyde, representing a mechanism which has the potential for a strong inhibition of reversion.

It was revealed in Chapter 5, however, that each mercaptan had resulted in a poor inhibition of the reversion of syringaldehyde. It was suggested that a removal mechanism involving quinone species may have been active, but in an alternating cycle with photo-oxidative yellowing reactions. In light of the poor inhibition which had been observed, it was suggested that the yellowing reactions were dominant, or the removal of the yellow species by the mercaptans may have occurred at a slow rate. The results presented in this section indicate that this is, indeed a possibility. This mechanism and its subsequent cycling was shown in Chapter 5, Figures 5.7 and 5.8, respectively.

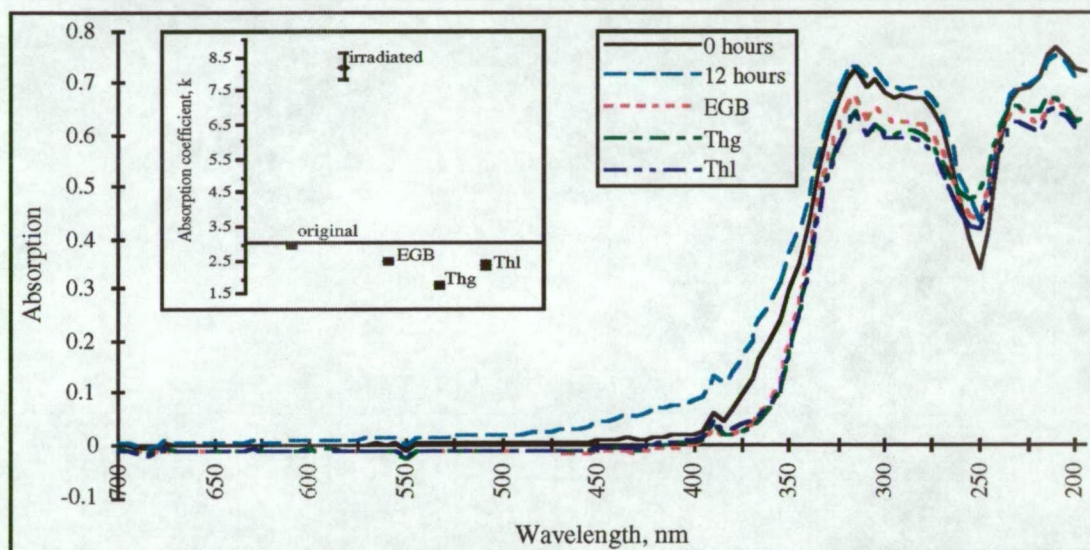
### *Vanillin*

The absorption coefficients,  $k$ , and UV-visible absorption spectra for vanillin before irradiation, after irradiation, and after subsequent treatment of the irradiated samples with the three mercaptans are presented in Figure 6.8.

The observations for irradiated vanillin treated with each mercaptan, presented in Table 6.2, indicated that only a small removal of coloured species had occurred, as the samples were all still strongly coloured after treatment. The absorption coefficients, shown in Figure 6.8, however, indicated that the chromophore content of the irradiated samples was removed to below the original non-irradiated state. The UV-visible absorption spectra also indicated this, as the increased absorption above 350nm caused by irradiation, (which includes a small broad peak centred around 420nm, and can be attributed to the formation of coloured quinone species, see Chapter 4), was removed by each mercaptan treatment. Furthermore, each mercaptan treatment had resulted in this absorption being reduced to below the corresponding absorption for the original non-irradiated sample. It is possible that



the removal reactions had continued in the solid phase on the filter paper while drying, affording a slow but larger colour removal than was previously observed. It is more likely, however, that the original non-irradiated sample contained some yellow quinone contaminants, which had been introduced by atmospheric oxidation prior to its measurements being taken, (this was discussed in Chapter 4). Therefore, the removal of coloured species to below the original state, revealed in Figure 6.8, could represent a removal of coloured products of photo-yellowing, along with a removal of atmospheric oxidation products which had formed prior to irradiation.



**Figure 6.8.** The absorption coefficients,  $k$  ( $\text{g}/\text{m}^2$ )<sup>-1</sup>, and UV-visible absorption spectra for vanillin prior to and after 12 hours of irradiation by Ultravitalux sunlamps, and after treatment of the irradiated samples with EGB, Thg and Thl.

At any rate, the removal of the coloured products of irradiation by each mercaptan indicates that these mercaptans contain the ability to impart a strong “removal” mechanism during the irradiation of vanillin. It was revealed in Chapter 5, however, that only a partial inhibition had occurred for treatments of vanillin with each mercaptan. It was suggested in Chapter 4 that vanillin and syringaldehyde underwent similar photo-reactions, both producing quinone species. It is possible that they have also undergone similar inhibitory processes, with removal-oxidation cycles being established (see syringaldehyde, above).

#### Quinone species:

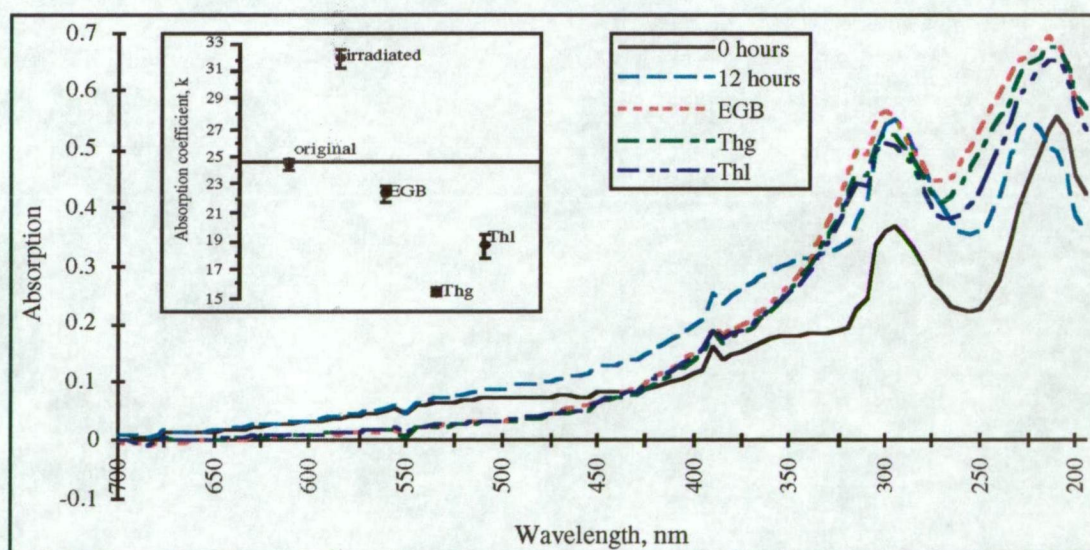
Observations of the colour changes in the quinone species, (1,4-benzoquinone, methoxyhydroquinone and methylhydroquinone), resulting from irradiation and subsequent treatment with each mercaptan are shown in Table 6.3.



**Table 6.3.** Observations of the colour changes quinone species, resulting from irradiation and subsequent treatment with each mercaptan.

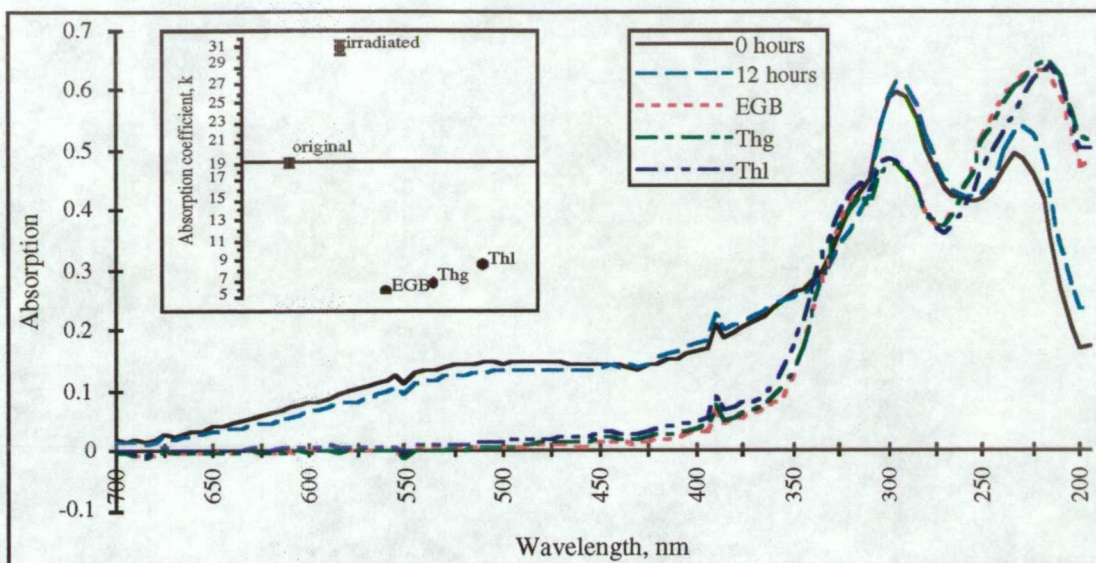
MLC, and its original colour	Colour of MLC after 12 hrs of irradiation	Mercaptan treatment	Colour of irradiated MLC after treatment
Methoxyhydroquinone: orange-brown	orange-red	EGB & Thl	orange
		Thg	light orange-yellow
Methylhydroquinone: colourless	orange-pink	EGB	pale yellow
		Thg	paler yellow
		Thl	pale orange
1,4-Benzoquinone: dark red	dark red-brown	EGB & Thl	dark orange
		Thg	light orange

It is apparent from this table that each mercaptan was able to significantly bleach each irradiated quinonoid species. For irradiated methoxyhydroquinone and 1,4-benzoquinone, this bleaching appeared to extend to below their original colour. Irradiated methylhydroquinone, on the other hand, was not bleached back to its originally colourless state. This is discussed below, along with changes in the absorption coefficients,  $k$ , and UV-visible absorption spectra for each irradiated quinonoid species treated with mercaptans. The absorption coefficients and absorption spectra are shown in Figures 6.9-6.11 for 1,4-benzoquinone, methoxyhydroquinone, and methylhydroquinone, respectively.

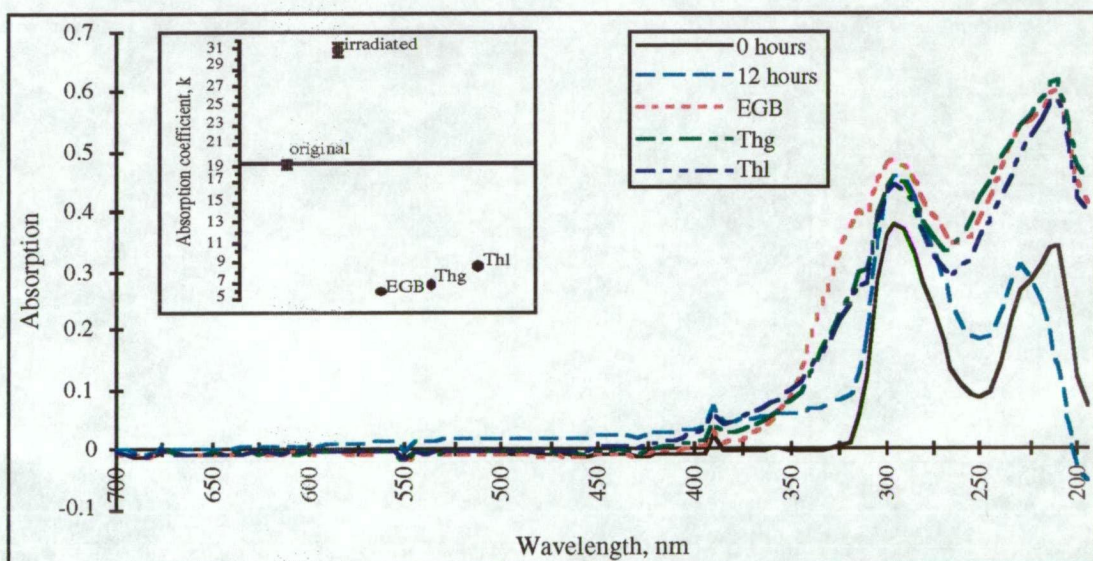


**Figure 6.9.** The absorption coefficients,  $k$  ( $\text{g/m}^2$ )<sup>-1</sup>, and UV-visible absorption spectra for 1,4-benzoquinone prior to and after 12 hours of irradiation by Ultravitalux sunlamps, and after treatment of the irradiated samples with EGB, Thg and Thl.





**Figure 6.10.** The absorption coefficients,  $k$  ( $\text{g/m}^2$ ) $^{-1}$ , and UV-visible absorption spectra for methoxyhydroquinone prior to and after 12 hours of irradiation by Ultravitalux sunlamps, and after treatment of the irradiated samples with EGB, Thg and Thl.



**Figure 6.11.** The absorption coefficients,  $k$  ( $\text{g/m}^2$ ) $^{-1}$ , and UV-visible absorption spectra for methylhydroquinone prior to and after 12 hours of irradiation by Ultravitalux sunlamps, and after treatment of the irradiated samples with EGB, Thg and Thl.

### *1,4-Benzoquinone and methoxyhydroquinone*

The large decreases, (to below the original values), in the absorption coefficients presented in Figures 6.9 and 6.10, indicate that each mercaptan treatment had reduced the chromophore content of each of these irradiated quinonoid species to below that of their corresponding original, non-irradiated samples. This is in

accordance with the observations of colour changes in Table 6.3 for 1,4-benzoquinone and methoxyhydroquinone. Results presented in Chapter 4 indicated that these two compounds had undergone atmospheric oxidation prior to irradiation, establishing a redox equilibrium consisting of corresponding quinone and hydroquinone species. Therefore, for both of these compounds, the decrease in colour and chromophore content of the irradiated samples to below their original values was likely to have been a result of a removal of coloured products of irradiation, along with a removal of quinone species that were present prior to irradiation.

The UV-visible absorption spectra revealed that each mercaptan had reduced all absorption above 350nm for both irradiated 1,4-benzoquinone (Figure 6.9) and irradiated methoxyhydroquinone (Figure 6.10). Included in this was a reduction in absorption at 360nm and 425nm, typical of quinone species. A broad peak centred at 525nm was also reduced for 1,4-benzoquinone, and removed for methoxyhydroquinone by each mercaptan treatment. This region is indicative of quinone dimerisation and cyclisation products, which were introduced in Chapter 4 as being products of irradiation of *p*-quinone species.

Therefore, it seems that for 1,4-benzoquinone and methoxyhydroquinone, each mercaptan had removed quinone species which had pre-existed in the samples, and quinone species which had been produced upon irradiation, along with their dimerisation and cyclisation products. It thus appears that each mercaptan contains the ability to strongly inhibit the reversion of these species via a "removal" mechanism.

The inhibition of reversion of 1,4-benzoquinone was not discussed in Chapter 5, but results presented for methoxyhydroquinone had revealed that only EGB and Thg were able to inhibit its reversion to a large degree. Thl treatment had afforded no inhibition at all, in fact it had even increased the photo-induced discolouration of methoxyhydroquinone. As discussed for syringaldehyde above, this could have been due to the establishment of a reduction-oxidation cycle during irradiation, with competing photo-yellowing reactions overwhelming the removal reactions.

### *Methylhydroquinone*

The observations presented in Table 6.3 indicated that bleaching was not complete after treating irradiated methylhydroquinone with each mercaptan. The decrease in the absorption coefficients presented in Figure 6.11, however, indicated that removal of chromophoric species had occurred to below the original state for each mercaptan

treatment. It is possible that removal reactions had continued on the filter paper medium prior to taking measurements.

The UV-visible absorption spectra for irradiated methylhydroquinone treated with each mercaptan revealed a decrease in absorption around 420nm (i.e. the region of a secondary absorption maxima for quinone species). Thus it is possible that each mercaptan had removed quinone species which had been produced upon irradiation of methylhydroquinone. A reduction in absorption in the region of the primary absorption peak for quinone species (360nm) was not observed, but this region was largely overlapped by an absorption peak at 330nm, which had been introduced upon treatment with each mercaptan. This peak was also observed for irradiated eugenol treated with each mercaptan, and, as with eugenol, it was also seen to have been introduced after treatment of the non-irradiated samples with each mercaptan (see Chapter 5). Therefore, this absorption peak could indicate the formation of a reaction product between methylhydroquinone and each mercaptan.

So, the results presented here indicate that, once again, each mercaptan contains the ability to remove coloured products as they are formed during irradiation. Chapter 5 revealed that EGB had increased the reversion of methylhydroquinone rather than inhibited it. Thus, if EGB had acted via a "removal" mechanism during the irradiation of this MLC in Chapter 5, it was certainly too slow to be effective against competing yellowing reactions. Thg and Thl were observed to have inhibited reversion to a large degree in Chapter 5, but this was not supported by the colour parameters and absorption coefficients. It was suggested that these two mercaptans had imparted an effective inhibition, which was active only in the presence of irradiation. It was further proposed that when irradiation had been stopped, post-storage reversion had occurred to an elevated degree. It is possible that these two mercaptans had effected a successful "removal" mechanism during the irradiation of methylhydroquinone, with the removed species being quickly re-generated during storage when the exposure had ended.

#### *In summary*

Each mercaptan was shown to contain the ability to impart a removal mechanism during irradiation of each MLC which had previously been shown to undergo varied extents of inhibition in Chapter 5. This ability was shown to be strong, (i.e. a complete or almost complete removal of irradiation-induced chromophores on mercaptan treatment had occurred), for each MLC except eugenol. For eugenol, only a small reduction of irradiation-induced chromophoric species had occurred by mercaptan treatment, so their ability to act via a removal mechanism would be weak and incomplete.



The varying efficiencies of inhibition which were observed in Chapter 5 could have been due to a competition between removal reactions and photo-yellowing reactions. These competing reactions could exist in a reduction-oxidation cycle of quinone irradiation products and their hydroquinone counterparts (as shown in Chapter 5, Figure 5.8). Different rates of each reaction in a particular MLC/mercaptan system may vary, resulting in different efficiencies of the overall inhibition.

#### 6.1.4 Conclusions

The capability of mercaptans to inhibit photo-induced reversion by removing the coloured products as they formed varied depending on both the mercaptan and the compound it was applied to. Four general responses were found and are listed below.

- *The potential for inhibition to occur mainly via a “removal” mechanism*

Evidence for this included a complete removal of photo-induced chromophoric products, along with a complete or strong inhibition previously established in Chapter 5. This was found to be the case for:

mercaptan	MLC
EGB	isoeugenol methoxyhydroquinone.
Thg	isoeugenol methoxyhydroquinone acetovanillone.
Thl	isoeugenol acetovanillone.

Thg and Thl acting on methylhydroquinone could also have imparted a strong “removal” mechanism, which was rapidly lost during post-storage when irradiation was removed.

EGB acting on irradiated TMP handsheets was also found to have completely removed the photo-induced chromophoric products. Therefore it is possible that the inhibition of reversion of TMP handsheets by EGB treatment (seen in Chapter 3) could also have occurred mainly via a “removal” mechanism.

- *A potential involvement of a “removal” mechanism, but in conjunction with other inhibition mechanisms*

Evidence for this included only a partial removal of chromophoric irradiation products, despite a complete or strong inhibition having been previously established in Chapter 5. This was found to be the case for each mercaptan studied while acting on guaiacol or vanillic acid.

- *The potential for a “removal” mechanism, with an overall inefficiency, possibly due to competing yellowing reactions being dominant*

Evidence for this included a partial or complete removal of photo-induced chromophoric products, with little or no inhibition having been previously established in Chapter 5. This was found to be the case for:

mercaptan	compounds
EGB	*eugenol vanillin syringaldehyde methylhydroquinone *acetovanillone.
Thg	*eugenol vanillin syringaldehyde.
Thl	*eugenol vanillin syringaldehyde methoxyhydroquinone.

\*Note that for these compounds, the potential ability for a “removal” mechanism was very weak, as the bleaching of the irradiated samples by the mercaptans was small. In fact, these compounds may just as easily have been placed in the next category.

In these cases inhibition via removal of yellow products as they were formed may have occurred, with yellowing reactions being dominant over the removal reactions. For example, the rate of the removal reactions may have been too slow compared to the rates of the yellowing reactions. Another possibility is that the mercaptans could have been consumed quickly during the removal reactions, with inhibition then ceasing after a complete depletion of active mercaptan species.

- A “removal” mechanism either not occurring, or only playing a minor role in inhibition

This was shown to be the case for EGB acting on peroxide bleached TMP handsheets. This conclusion was based on the inability of EGB to significantly remove the photo-induced yellow products from irradiated BTMP, despite it having been previously shown to have inhibited the photo-reversion of BTMP.

## **6.2 Inhibition of Sensitised Reactions as a Way of Inhibiting Reversion**

### **6.2.1 Introduction**

Chapter 1, Section 1.2, reported the involvement of sensitiser groups in the early stages of photo-induced reversion. Sensitiser groups include  $\alpha$ -carbonyl groups, C=C groups and some others. It is suspected that such groups are able to absorb UV radiation, become excited and then initiate further reactions that lead to coloured products. Deactivating these sensitiser groups has been explored as a possible way of inhibiting reversion. As discussed in Section 1.3, inhibition directed at these groups has been tried by chemically modifying the carbonyl group with, for example, borohydride reduction, or quenching the excited  $\alpha$ -carbonyl state by applying excited state quenchers. Although mercaptans have not previously been linked to such a mode of inhibition, with radical quenching being a more generally accepted mechanism, little is actually known about their mode of action.

Results from Chapter 5 suggested that mercaptans may exhibit a range of inhibitory actions, depending on both the mercaptan used and the compound they are acting upon. It is suspected, therefore, that their range of inhibition mechanisms is more diverse than previously discussed in Section 1.3. This section is intended to gauge the possibility of mercaptans exerting an inhibitory effect directed towards sensitisation steps. The experiment involved adding sensitisers to model lignin compounds, and seeing if mercaptans could inhibit any enhanced photo-yellowing induced by the sensitiser presence.

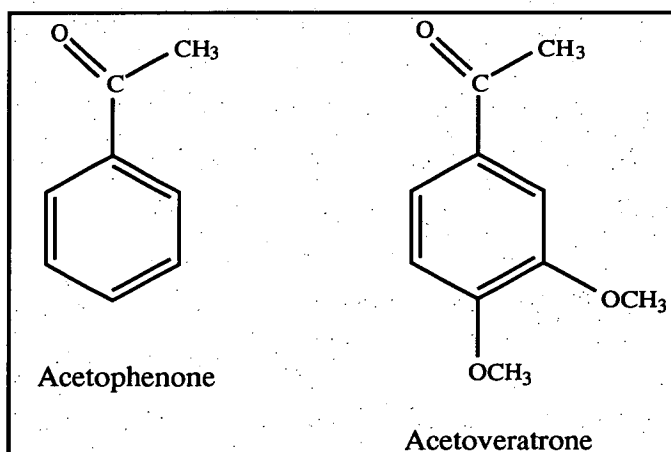
For simplicity, only EGB was tested on the photo-sensitisation of three model lignin compounds studied in Chapters 4 and 5, which had revealed different histories with respect to both their reversion and their inhibition by EGB treatment. These compounds are listed below:

1. Guaiacol, a Category 2 compound, (experiencing reversion manifesting as darkening and yellowing with no change in the red-green colour co-ordinate  $a^*$ , see Chapter 4). Complete inhibition of photo-induced reversion was found for EGB treatment (see Chapter 5). The previously studied “removal” mechanism (see Section 6.1) was found as a possible partial mechanism.

2. Vanillin, also a Category 2 compound (Chapter 4), but unlike guaiacol had revealed only a small photo-reversion inhibition by EGB treatment in Chapter 5. The previously studied “removal mechanism” (see Section 6.1) was found to have potential, with dominating yellowing reactions.

3. Methoxyhydroquinone, a Category 3 compound, (experiencing reversion manifesting as darkening, yellowing and a change in the red-green colour co-ordinate  $a^*$ , see Chapter 4). Along with an initial bleaching, this compound had experienced an almost complete inhibition of photo-induced reversion by treatment with EGB in Chapter 5. The previously studied “removal mechanism” (see Section 6.1) enabled a major, if not complete, role in inhibition.

In order to test for the possibility of EGB to interfere with sensitisation steps in the photo-yellowing reactions two photo-sensitisers, both obtained from Aldrich Chemicals, were studied. Acetophenone (S1) (a colourless liquid, 99% MW 120.15) is used in organic synthesis as a photo-sensitiser (Merck Index 10th ed.). Acetoveratrone (S2) or 3,4-dimethoxyphenyl acetone (a viscous pale yellow liquid, 97%, MW 194.23) has been studied by Agnemo et al<sup>66</sup>. They found that although it did not yellow upon irradiation, and indeed was recoverable after irradiation, it still enhanced the photo-induced yellowing of a model lignin compound, i.e. it behaved as a photo-sensitiser. Structures of these sensitisers are shown in Figure 6.12.



**Figure 6.12.** Photo-sensitisers used in the study.

Each photo-sensitiser was added to duplicate samples of the MLCs, with one set treated with EGB, and then irradiated. Sensitisation, or enhancement of the photo-yellowing was monitored, along with the effect EGB had on these processes.

## 6.2.2 Specific Methods

All solutions contained 0.5% concentrations of each compound in DMF. Irradiation was performed for 12 hours as previously described in Chapter 4. Adsorption onto filter paper, and subsequent measurements and calculations were also done following the procedures described in Chapter 4.

## 6.2.3 Results and Discussion

### Sensitiser controls

The absorption coefficients,  $k$ , before and after irradiation of the two sensitisers, (with and without EGB), are shown in Table 6.4. The UV-visible absorption spectra for these treatments are shown in Figures 6.13 and 6.14 for acetophenone (S1) and acetoveratrone (S2), respectively. All solutions were colourless prior to and after irradiations.

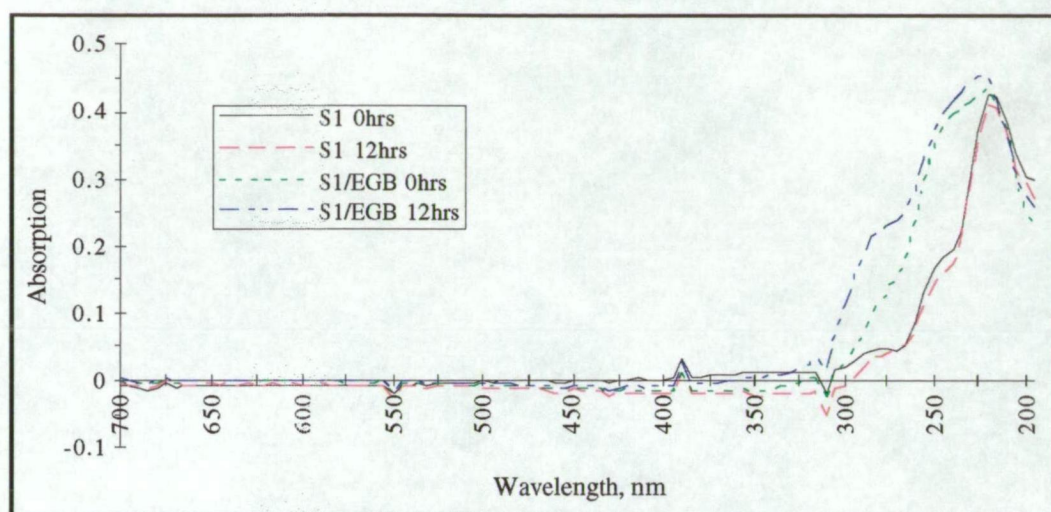
**Table 6.4.** The absorption coefficients,  $k$  ( $\text{g/m}^2$ )<sup>-1</sup>, for the sensitisers acetophenone (S1) and acetoveratrone (S2) treated with the mercaptan EGB, and then irradiated for 12 hours by Ultravitalux sunlamps.

sensitiser	EGB	0 hours	12 hours	$\Delta k_{(12\text{-hrs})}$
S1	-	1.1	0.9	-0.2
S1	+	1.0	0.9	-0.1
S2	-	0.8	0.9	0.1
S2	+	1.0	0.9	-0.1

Note that the standard deviations were  $\pm 0.1$  in each case.

As expected for a photo-sensitiser compound, no significant changes in the absorption coefficient occurred as a result of irradiation for both acetophenone (S1) and acetoveratrone (S2) in the absence or presence of EGB. That is, no photo-induced chromophore production was detected.

## Acetophenone



**Figure 6.13.** UV visible absorption spectra for acetophenone treated with EGB and irradiated for 12 hours by Ultravitalux sunlamps.

For acetophenone in the absence of EGB, the UV-visible absorption spectra (Figure 6.13) confirms that no significant changes had occurred as a result of irradiation.

On treatment of the non-irradiated sample with EGB, increases in absorption between 220 and 300nm were similar to the spectra observed for EGB alone (see Chapter 5, Figure 5.1). They are therefore likely to be a result of the presence of EGB, and not indicative of interactions between EGB and the sensitizer.

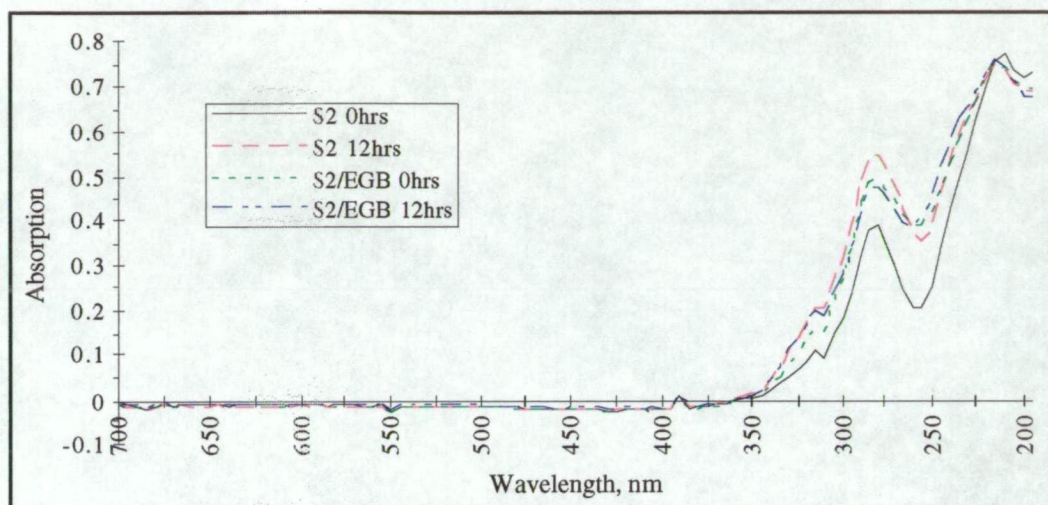
On irradiation of the EGB treated sample, increases in absorption were also similar to those found in Chapter 5 for EGB alone, except for an increase in an absorption shoulder at 285nm. In Chapter 5 it was suggested that the small changes in the UV-visible absorption spectra for EGB on irradiation could have arisen from some photo-activity about the C=O groups, or by the formation of disulphide bonds and dimers. It is possible that acetophenone has enhanced the photo-activity of EGB about its C=O groups (which absorb around 285nm). Alternatively, EGB may have increased the photo-activity around the C=O group of acetophenone.

## Acetoveratrone

For acetoveratrone (Figure 6.14), a hyperchromic effect was observed between 220 and 340nm by all treatments (i.e. treatment with EGB and irradiations). Included in this hyperchromic effect was an increase in the intensity of the 280nm peak of acetoveratrone, where C=O groups absorb. Therefore both EGB treatment and irradiation may have similarly increased activity about the C=O group of



acetoveratrone. No absorption peaks were removed, introduced, or shifted, so it appears that no chemically altering reactions had occurred.



**Figure 6.14.** UV visible absorption spectra for acetoveratrone treated with EGB and irradiated for 12 hours by Ultravitalux sunlamps.

## Model lignin compounds

### *Guaiacol*

Observations and the absorption coefficients,  $k$ , for guaiacol treated with the sensitisers, EGB and irradiated are shown in Table 6.5. The UV-visible absorption spectra for acetophenone (S1) and acetoveratrone (S2) treatments are shown in Figures 6.15 and 6.16 respectively. The corresponding spectra for the unsensitised photo-reversion of guaiacol and its inhibition by EGB were shown in Chapters 4 and 5 (see Figures 4.12, 5.2a and 5.2b), and comparisons made below refer to these figures.

On treatment of guaiacol with acetoveratrone, a small increase in  $k$  was initially observed. However, this was likely to have been due to the small yellow tinge of acetoveratrone alone.

Upon irradiation, both acetophenone (S1) and acetoveratrone (S2) have increased the absorption coefficient of guaiacol to a much greater extent than in their absence. Thus it appears that they have both behaved as highly efficient photo-sensitisers for the photo-induced reversion of guaiacol, with acetophenone being the more efficient of the two.

**Table 6.5.** Observations and absorption coefficients,  $k$  ( $\text{g/m}^2$ )<sup>-1</sup>, for guaiacol treated with the sensitisers acetophenone (S1) and acetoveratrone (S2), the mercaptan EGB, and then irradiated for 12 hours by Ultravitalux sunlamps.

sensitiser	EGB	0 hours	12 hours	$\Delta k_{(12-0\text{hrs})}$
-	-	1.0	1.8 pale orange	0.8
-	+	1.0	0.9 colourless	-0.1
S1	-	0.9	5.2 orange	4.3
S1	+	0.9	4.9 light orange	4.0
S2	-	1.3	4.4 orange	3.1
S2	+	1.1	1.5 yellow tinge	0.4

Note that all solutions were colourless prior to irradiation, and that standard deviations in the absorption coefficient were  $\pm 0.1$  in each case.

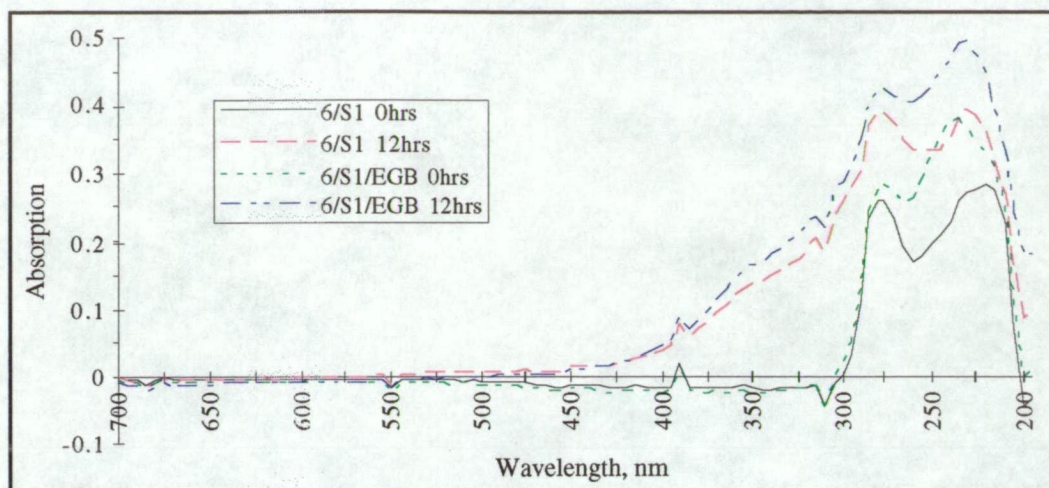
In Chapter 5 it was shown that EGB completely inhibited the photo-reversion of guaiacol. In the presence of acetophenone, however, EGB was not able to inhibit the sensitised reversion of guaiacol (as the increase in the absorption coefficient on irradiation, shown in Table 6.5, was almost as high as that for the sensitised and irradiated sample).

In the presence of acetoveratrone, EGB was able to inhibit the sensitised reversion. In fact, this inhibition was almost as efficient as the inhibition that was observed by EGB in the absence of a sensitiser. This was shown in Table 6.5, as the absorption coefficient had increased only slightly upon irradiation for the acetoveratrone-EGB treated sample.

#### *Spectral changes for acetophenone treatments*

For acetophenone, the UV-visible absorption spectra (Figure 6.15) revealed no initial interactions between acetophenone and guaiacol as, (apart from the presence of a small shoulder at 245nm, which was just due to the presence of acetophenone), this spectrum is identical to that of guaiacol alone (see Chapter 4).





**Figure 6.15.** UV visible absorption spectra for guaiacol treated with acetophenone and EGB and then irradiated for 12 hours by Ultravitalux sunlamps.

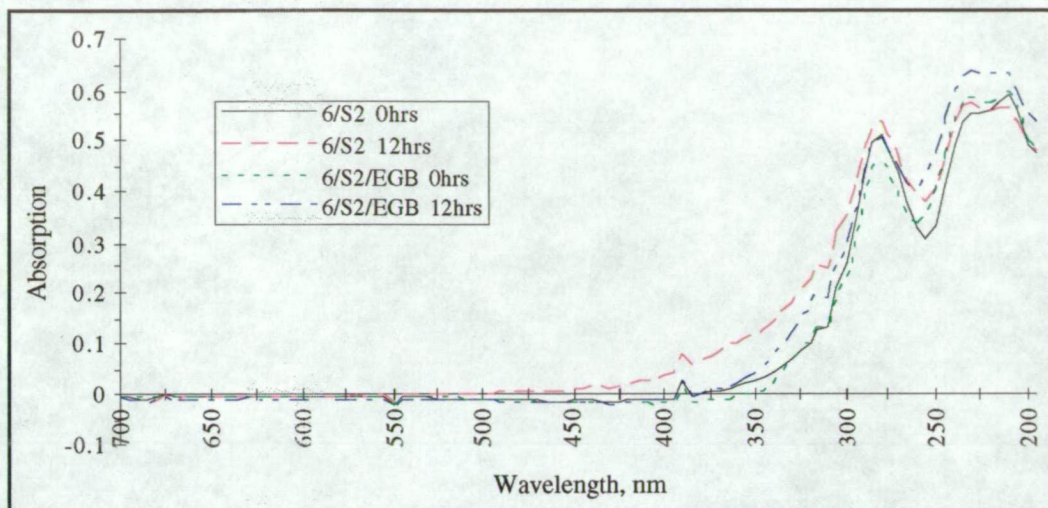
Upon irradiation, the spectrum was also identical to that of irradiated guaiacol alone (see Chapter 4), but with increased intensities, especially about the broad 350nm peak resulting from the production of yellow species. Therefore, the UV-visible absorption spectra has confirmed that acetophenone has not altered the photochemistry of guaiacol, but indeed has enhanced the production of yellow species greatly, that is, it has behaved as a photo-sensitiser.

In Chapter 5, EGB was shown to inhibit completely the formation of this yellowing peak at 350nm by irradiation. In Figure 6.15 it is apparent that EGB has been unable to inhibit the formation of this peak in the presence of acetophenone, in fact it seems to have increased it slightly with respect to the sensitised and irradiated sample. Therefore, in this case, not only has EGB been unable to inhibit the photo-sensitisation reactions, it has also had its previously shown inhibition ability destroyed.

#### *Spectral changes for acetoveratrone treatments*

The UV-visible absorption spectra for guaiacol treated with acetoveratrone (Figure 6.16) revealed that a broad, small peak had been introduced at 315nm which could represent some yellow colouration. This is not necessarily due to any interactions having taken place, however, as it is similar to the spectra for acetoveratrone alone (see Figure 6.13), and is consistent with the slight yellow colouration of acetoveratrone itself.





**Figure 6.16.** UV visible absorption spectra for guaiacol treated with acetoveratrone and EGB and then irradiated for 12 hours by Ultravitalux sunlamps.

As with acetophenone discussed above, an increase in absorption of the acetoveratrone treated sample around 350nm on irradiation is consistent with guaiacol alone upon irradiation, once again with an enhanced intensity. This confirms that, like acetophenone, acetoveratrone has also acted as a photo-sensitiser in the photo-reversion of guaiacol.

The presence of EGB has not altered the initial curve with respect to the sensitiser-guaiacol one. On irradiation the production of yellowing species absorbing at 350nm has been greatly reduced, but not completely inhibited. Therefore, although EGB has inhibited the sensitiser-enhancement of photo-reversion in this case, its complete inhibition ability in the absence of a photosensitiser, which had previously been observed in Chapter 5, has been diminished.

### *In conclusion*

Both acetophenone and acetoveratrone sensitised the photo-reversion of guaiacol. While EGB was able to inhibit this sensitisation by acetoveratrone, it had little effect on the sensitisation by acetophenone.

### *Vanillin*

Observations and the absorption coefficients,  $k$ , for vanillin treated with the sensitisers, EGB and irradiated are shown in Table 6.6. The UV-visible absorption spectra for acetophenone (S1) and acetoveratrone (S2) treatments are shown in Figures 6.17 and 6.18 respectively. The corresponding spectra for the unsensitised photo-reversion of vanillin and its inhibition by EGB were shown in Chapters 4 and 5 (see Figures 4.15, 5.6a and 5.6b), and comparisons made below refer to these figures.

**Table 6.6.** Observations and absorption coefficients,  $k$  ( $\text{g/m}^2$ )<sup>-1</sup>, for vanillin-treated with the sensitisers acetophenone (S1) and acetoveratrone (S2), the mercaptan EGB, and then irradiated for 12 hours by Ultravitalux sunlamps.

sensitiser	EGB	0 hours	12 hours	$\Delta k_{(12-0\text{hrs})}$
-	-	3.0	$8.2 \pm 0.4$ light orange	$5.2 \pm 0.4$
-	+	1.1	3.7 dark yellow	2.6
S1	-	3.3	4.8 light orange	1.5
S1	+	1.2	2.8 yellow	1.6
S2	-	2.7	10.8 light orange	8.1
S2	+	1.1	3.6 yellow	2.5

Note that all solutions were colourless prior to irradiation. Standard deviations were  $\pm 0.1$  unless stated otherwise

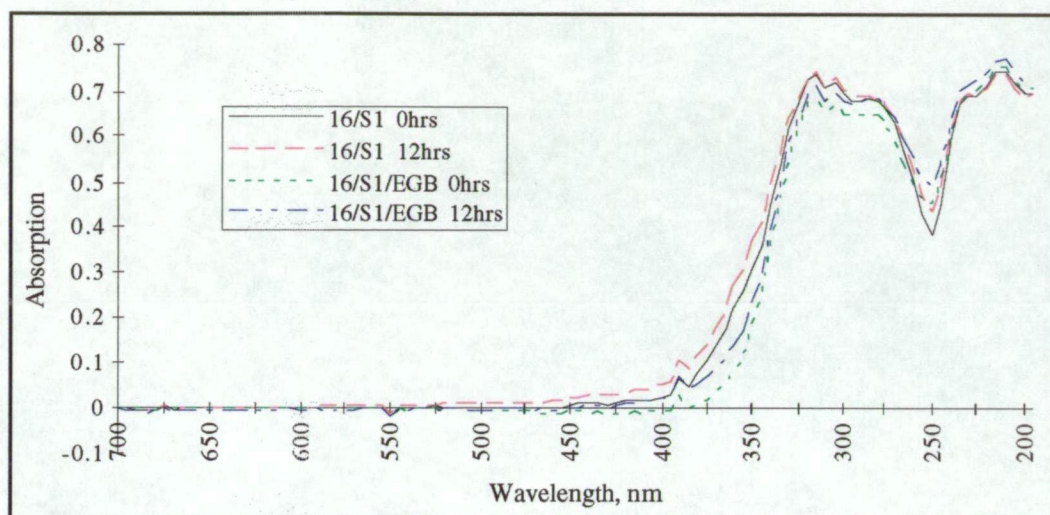
For the non-irradiated samples, the lower  $k$  values for all EGB treated samples was likely to have been a result of a removal of atmospheric oxidation products of vanillin, as discussed previously in Chapter 5.

Acetophenone (S1) did not reveal any photo-sensitising ability in the photo-yellowing reactions of vanillin, as the increase in the absorption coefficient was no greater on irradiation than that observed for vanillin alone. In fact, the rise in the absorption coefficient on irradiation in the presence of acetophenone was *less than* in its absence, thus it appears to have actually inhibited the reversion to a small extent. Acetoveratrone (S2), on the other hand, did enhance the increase in the absorption coefficient, and therefore the photo-yellowing, to a small degree.

For acetophenone, the presence of EGB did not significantly alter the change in the absorption coefficient after irradiation, so therefore it had not affected the action of acetophenone on vanillin during irradiation.

For vanillin treated with acetoveratrone in the presence of EGB, irradiation resulted in a similar rise in the absorption coefficient as was seen for the unsensitised EGB treated sample. Therefore, for acetoveratrone it appears that EGB, although still unable to completely inhibit the reversion of vanillin, was able to inhibit the sensitisation of this photo-reversion.





**Figure 6.17.** UV visible absorption spectra for vanillin treated with acetophenone and EGB and then irradiated for 12 hours by Ultravitalux sunlamps.

For vanillin treated with acetophenone the UV-visible absorption spectra (Figure 6.17) was identical to the spectra for vanillin alone (see Chapter 5). Therefore, no chemically altering reactions have occurred as a result of acetophenone addition.

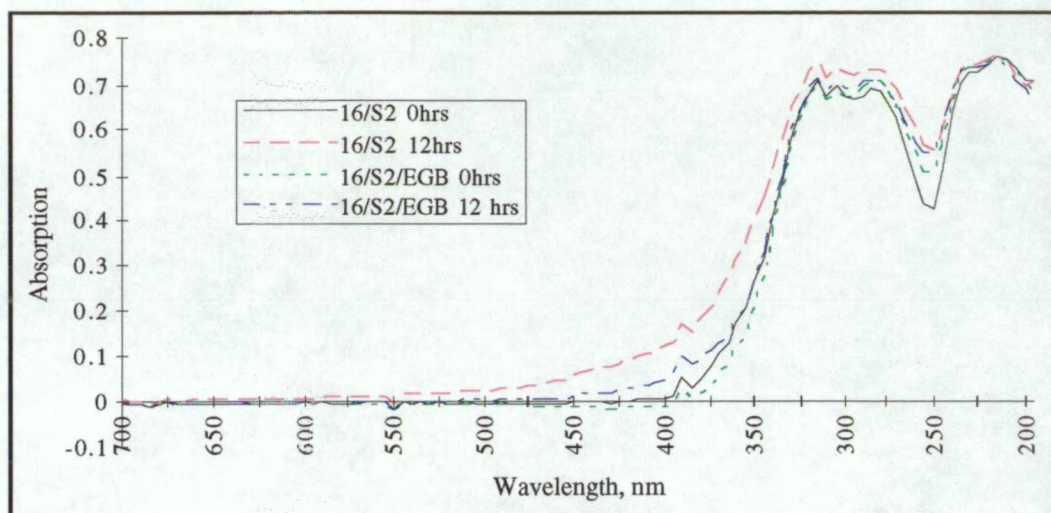
A small increase in absorption greater than 350nm on irradiation of the acetophenone treated vanillin sample was also consistent with the spectra for irradiated vanillin alone (Chapter 4). Therefore, the UV-visible absorption spectra supports that acetophenone had not enhanced the reversion processes of vanillin.

For the spectra of vanillin treated with EGB and acetophenone, a removal of small activity around 400nm can be seen. This is also consistent with the spectra for vanillin treated with EGB, shown in Chapter 5, which was attributed to the removal of atmospheric oxidation products of vanillin.

Upon irradiation, a small increase in absorption greater than 350nm was observed, which again was consistent with the spectra for vanillin treated with EGB and irradiated in Chapter 5.

Therefore, the UV-visible absorption spectra indicate that acetophenone had not affected the reversion processes of vanillin, or the inhibition of those processes by EGB.





**Figure 6.18.** UV visible absorption spectra for vanillin treated with acetoveratrone and EGB and then irradiated for 12 hours by Ultravitalux sunlamps.

The UV-visible absorption spectra for vanillin treated with acetoveratrone (Figure 6.18) was also identical to the spectra of vanillin alone (see Chapter 4), therefore acetoveratrone has effected no chemically altering reactions in vanillin.

Irradiation induced similar changes in the spectra to those noted for the acetophenone treated samples discussed above, except that the increase in absorption above 350nm was enhanced by presence of acetoveratrone. Therefore, acetoveratrone has behaved as a photo-sensitiser for irradiated vanillin.

The spectra of the irradiated sensitised sample treated with EGB reveal that EGB had inhibited this enhanced increase in absorption, but only partially. Therefore, the UV-visible absorption spectra confirmed that EGB had interfered with the small increase in photo-reversion induced by acetoveratrone.

### *In conclusion*

Acetoveratrone sensitised the photo-reversion of vanillin, and EGB was able to inhibit this sensitisation. Acetophenone, on the other hand, did not sensitise the reversion of vanillin. In fact, it appeared to have inhibited it. EGB had no effect on this.

## Methoxyhydroquinone

Observations and the absorption coefficients,  $k$ , for methoxyhydroquinone treated with the sensitisers, EGB and irradiated are shown in Table 6.7. The UV-visible absorption spectra for acetophenone (S1) and acetoveratrone (S2) treatments are shown in Figures 6.19 and 6.20 respectively. The corresponding spectra for the unsensitised photo-reversion of methoxyhydroquinone and its inhibition by EGB were shown in Chapters 4 and 5 (see Figures 4.17, 5.10a and 5.10b), and comparisons made below refer to these figures.

**Table 6.7.** Observations and absorption coefficients,  $k$  ( $\text{g/m}^2$ )<sup>-1</sup>, for methoxyhydroquinone treated with the sensitisers acetophenone (S1) and acetoveratrone (S2), the mercaptan EGB, and then irradiated for 12 hours by Ultravitalux sunlamps.

sensitiser	EGB	0 hours	12 hours	$\Delta k_{(12-0\text{hrs})}$
-	-	$19.1 \pm 0.3$ orange-brown	$31.0 \pm 0.7$ orange-red	$11.9 \pm 0.8$
-	+	$1.7 \pm 0.1$ brown tinge	$2.4 \pm 0.1$ dark orange	$1.7 \pm 0.1$
S1	-	$17.4 \pm 0.2$ orange-brown	$47.7 \pm 0.7$ orange-red	$30.3 \pm 0.7$
S1	+	$1.9 \pm 0.1$ pale yellow-brown	$80 \pm 17$ dark orange-red	$78 \pm 17$
S2	-	$37 \pm 2$ red-brown	$54 \pm 4$ dark orange-red	$17 \pm 4$
S2	+	$3.1 \pm 0.1$ pale brown	$67 \pm 7$ dark red	$64 \pm 7$

For the non-irradiated samples, acetophenone (S1) did not significantly affect the absorption coefficient of methoxyhydroquinone, nor does it appear to have affected the bleaching ability of EGB.

Acetoveratrone (S2), on the other hand, had increased the absorption coefficient greatly. In Chapter 4, it was proposed that the methoxyhydroquinone sample existed as an equilibrium atmospheric oxidation-reduction / hydroquinone-quinone solution, and that the bleaching observed by EGB could have been a result of EGB donating hydrogen to the system, pushing the equilibrium towards a higher content of hydroquinone species over the coloured quinones. It is possible that acetoveratrone had the opposite effect, with more oxidation favoured and therefore a higher initial quinone content. On addition of EGB to the acetoveratrone-methoxyhydroquinone sample, a strong bleaching was observed, and although the chromophore content was not restored to the amount for methoxyhydroquinone and EGB alone, it was reduced *more efficiently* in the presence of the photo-sensitiser. Thus, the presence of acetoveratrone did not diminish the bleaching ability of EGB. A competition

between the darkening effect of the sensitiser and the bleaching effect of EGB may have existed, with the bleaching dominating.

Upon irradiation, both acetophenone and acetoveratrone enhanced the increase in the absorption coefficient, with acetophenone being more efficient. Therefore, it appears that they both sensitised the photo-yellowing reactions of methoxyhydroquinone.

In the presence of EGB, this photo-reversion enhancement was driven even further, as the absorption coefficients for the irradiated EGB-treated sensitised samples were greatly elevated with respect to all other samples. Therefore, not only was EGB unable to inhibit the photo-sensitisation of methoxyhydroquinone, it also appears to have had its previously shown inhibition ability (see Chapter 5) completely destroyed while actually increasing photo-reversion reactions in the presence of the two photo-sensitisers. In Chapter 5, observations of the ability of mercaptans to inhibit photo-reversion of quinonoid compounds indicated that the pre-existence of quinone species may have aided the inhibition. It was also suggested that EGB may have irreversibly removed these species prior to irradiation, preventing them from being reformed. It is possible that the presence of the photo-sensitisers may have lowered the activation energy of the photo-induced quinone reformation, making this reaction possible. It is also possible that, in this case, EGB may have increased the photo-activity of the C=O groups of both sensitisers during irradiation, thereby enhancing their sensitising abilities (see 'sensitiser controls', discussed previously).

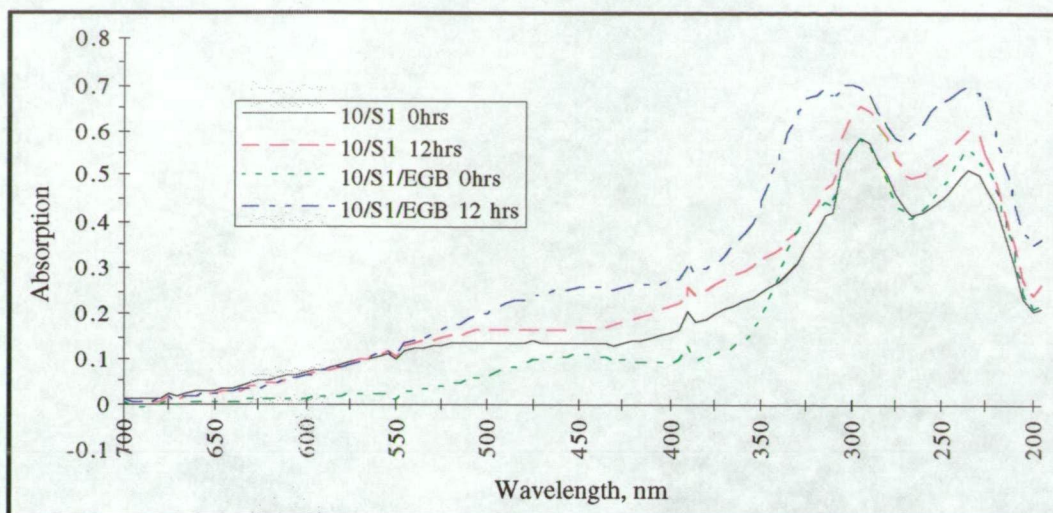
#### *Spectral changes for acetophenone treatments*

The UV-visible absorption spectra for methoxyhydroquinone treated with acetophenone (Figure 6.19) is identical to that of methoxyhydroquinone alone (see Chapter 4). Therefore, acetophenone has not appeared to have interacted with methoxyhydroquinone.

Irradiation of the sensitised sample resulted in a hyperchromic effect in all regions of the spectra (except for 550nm and above), so it is possible that acetophenone has enhanced the production of yellow species without chemically altering the reaction pathways.

In Chapter 5, EGB acting on methoxyhydroquinone alone was shown to have removed all absorption above 360nm, and this removal was shown to have been sustained during irradiation. This indicated the high efficiency of EGB in both bleaching methoxyhydroquinone and inhibiting its photo-induced reversion. In the presence of acetophenone, however, the initial absorption removal was incomplete, particularly around 445nm. Therefore, the bleaching ability of EGB appears to have been diminished.





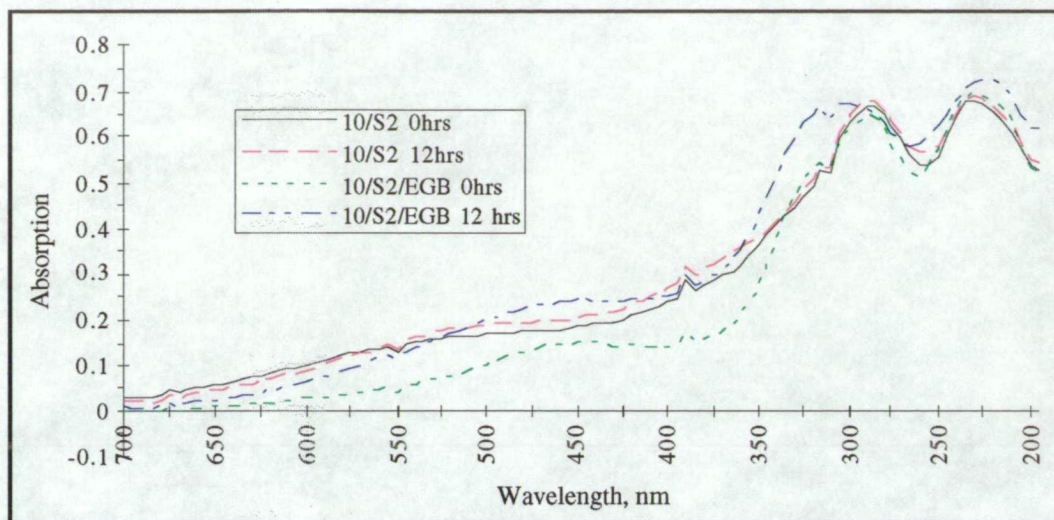
**Figure 6.19.** UV visible absorption spectra for methoxyhydroquinone treated with acetophenone and EGB and then irradiated for 12 hours by Ultravitalux sunlamps.

On irradiation of this EGB treated sensitised sample, absorption at 525nm was replenished to the original state, while all other absorption above 300nm exceeded even that of the irradiated sensitised sample. This confirms that the presence of EGB with acetophenone had not only failed to inhibit the formation of the photo-induced yellow products (which were likely to have been quinones, see Chapter 4), but had actually increased it. Therefore, EGB has definitely not inhibited photo-sensitisation in this case. These results also support the previously suggested proposal (see Chapter 5), that efficient initial bleaching was required for inhibition of this compound, and that a removal of coloured species as they were formed was a possible mode of action.

#### *Spectral changes for acetoveratrone treatments*

The UV-visible absorption spectra for the action of acetoveratrone on the photo-induced reversion of methoxyhydroquinone, and the bleachability and inhibition ability by EGB, (Figure 6.20) revealed changes identical to those discussed above for acetophenone. The only difference was that the enhanced absorption found for methoxyhydroquinone in the presence of both EGB and acetophenone upon irradiation was less in the presence of acetoveratrone and EGB. Thus, in the presence of acetoveratrone, EGB was also unable to inhibit the photo-induced reversion of methoxyhydroquinone, and even enhanced its sensitisation.





**Figure 6.20.** UV visible absorption spectra for methoxyhydroquinone treated with acetoveratrone and EGB and then irradiated for 12 hours by Ultravitalux sunlamps.

### *In conclusion*

Both acetophenone and acetoveratrone sensitised the reversion of methoxyhydroquinone. Acetoveratrone had even enhanced discolouration prior to irradiation. Therefore, it may have sensitised oxidation reactions of methoxyhydroquinone to methoxyquinone even in the absence of light. EGB was still able to bleach methoxyhydroquinone in the presence of both sensitisers, but not as efficiently as when it is on its own. Upon irradiation in the presence of these sensitisers, EGB not only failed to inhibit the sensitised reversion, but actually increased it.

### **6.2.4 Conclusions**

- Once again the ability of EGB to inhibit was varied. Inhibition of photo-sensitisation varied depending on both the photo-sensitiser involved and the model lignin compound acted upon.
- Acetophenone sensitised the photo-reversion of two out of the three model lignin compounds (guaiacol and methoxyhydroquinone), and in each case EGB was unable to inhibit this sensitisation. Therefore for the photo-sensitiser acetophenone, EGB has no ability to interfere with sensitisation. The presence of this photo-sensitiser even destroyed EGB's previously shown inhibition abilities. For methoxyhydroquinone at least this could be due to the sensitiser reducing the ability of EGB to remove coloured species as they form, or its efficiency in doing so.

- Acetoveratrone acted as a sensitiser in the photo-reversion of all three model lignin compounds studied. EGB was able to inhibit this sensitisation completely for guaiacol, although its previously shown photo-reversion inhibition ability was slightly diminished. For vanillin a partial inhibition of sensitisation by EGB was revealed. For methoxyhydroquinone not only was EGB ineffective in inhibiting the sensitisation by acetoveratrone, its previously shown bleaching ability was diminished and its previously shown inhibition of photo-reversion was completely destroyed by the presence of this photo-sensitiser.
- Therefore while mercaptans are able to interfere with photo-sensitisation in some cases, they have a detrimental effect, even increasing sensitisation in others.

A summary of the results obtained by this study is shown in Table 6.8.

**Table 6.8.** The effects of acetophenone- and acetoveratrone-sensitisation on the photo-reversion of model lignin compounds and its inhibition by EGB.

Model lignin compound	Acetophenone		Acetoveratrone	
	sensitisation	inhibition by EGB	sensitisation	inhibition by EGB
Guaiacol	+	-	+	+
Vanillin	-	-	+	+
Methoxyhydroquinone	+	-	+	-

## **6.3 UV-Absorption Mechanism**

### **6.3.1 Introduction**

Chapter 5 revealed, particularly for EGB, that mercaptans may undergo an initial response to UV radiation, possibly resulting in the formation of dimers. This observation prompted an investigation in this section into the possibility of the mercaptans interacting with UV radiation, and thus “shielding” the MLC from UV-induced reactions. A test was designed to see if the mercaptans were able to shield the MLC from UV radiation by absorbing the radiation prior to it reaching the MLC. This involved modifying the previous irradiation apparatus, in such a way that the UV radiation had to pass through a “jacket” containing the mercaptans, which surrounded a solution of MLC. If yellowing reactions were inhibited by this set-up,

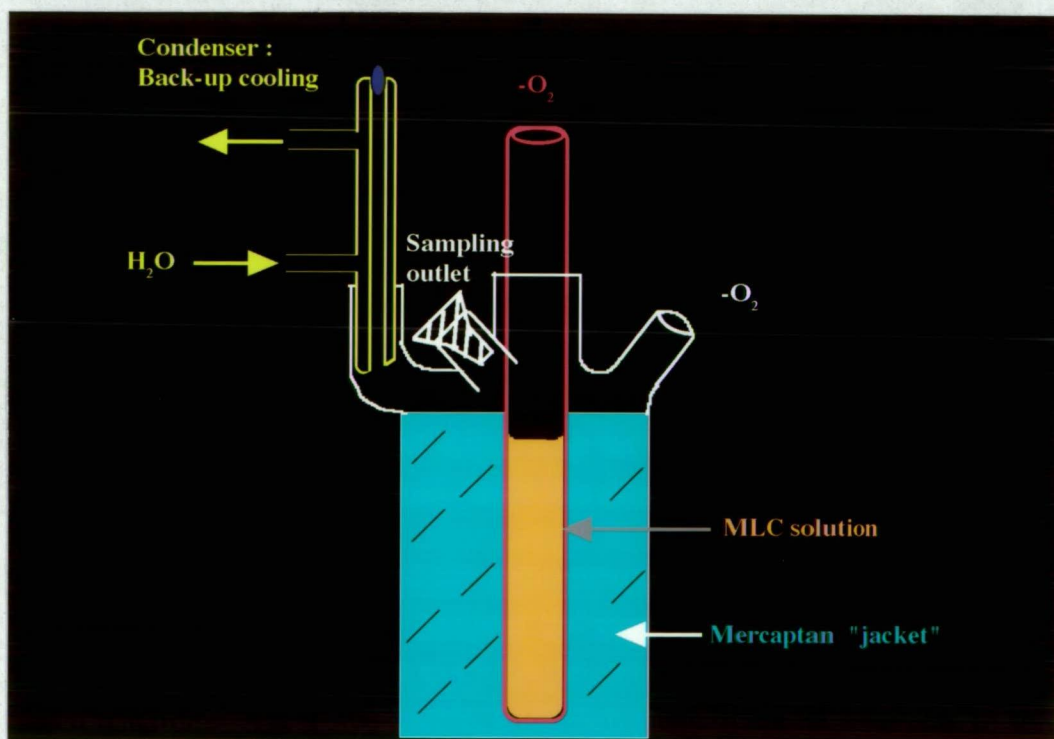


then it could be concluded that the mercaptans do indeed have a UV-absorbing function as a mode of reversion inhibition. The three mercaptans studied previously were tested on guaiacol, vanillin and methoxyhydroquinone only, for the same reasons as discussed in the previous section (Section 6.2).

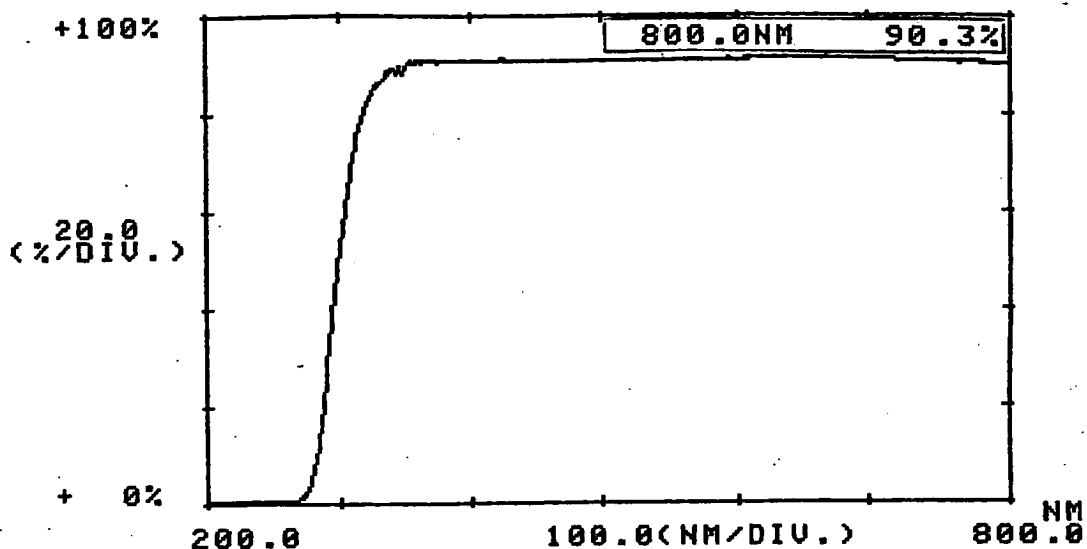
### 6.3.2 Experimental

#### Irradiation apparatus design, and heat interference test

The “jacket” apparatus is shown in Figure 6.21. The chambers containing the mercaptan “jacket” solutions were identical to those used in Chapter 4, but the cold finger was replaced with vessels containing the MLC solutions. These vessels were constructed using similar glass to the external chamber, albeit a different brand (Duran brand, compared to Pyrex brand for the external chamber). This did not present a problem, though, as the UV-visible transmittance spectra of this vessel (shown in Figure 6.22), revealed identical transmittance of light to that of the external chamber shown in Chapter 4 (see Figure 4.2).



**Figure 6.21.** The set-up used in the “jacket” experiment in which solutions of MLC are surrounded by, but not in contact with, mercaptan solutions during irradiation.



**Figure 6.22.** The UV-visible transmittance spectrum for the inner reaction vessel used in the “jacket” set-up shown in Figure 6.22.

The loss of the cold finger in the “jacket” set-up introduced the possibility of heat interference. The condenser was still present, however this did little in preventing overheating, as its main function was simply to prevent loss of solute in the event of overheating. Temperature readings of the MLC solutions within the internal vessel had revealed it to be adequately insulated from excessive temperature increases. The outer “jacket” solutions, however, experienced rises in temperature comparable to the heat emitted by the Ultravitalux lamps (see Chapter 2). Thus, the mercaptan solutions were also independently subjected to heat to gauge their reactions to it. This was done by placing  $0.5 \pm 0.2\%$  solutions of the mercaptans in DMF in a glass beaker, which was then placed on a hot plate with a range of  $50\text{--}60^\circ\text{C}$  for time periods identical to those for irradiation. A beaker containing  $\text{H}_2\text{O}$  was placed on top of the beakers containing the mercaptan solutions to prevent evaporation, while leaving a small gap for ventilation. Samples and measurements were taken as previously described in Chapter 4. The results of these tests will be discussed later.

### **Irradiation and measurements**

Irradiations were performed for a total of 12 hours, with intervals of cooling as previously described in Chapter 4. 5ml of  $0.5 \pm 0.1\%$  MLC in DMF solutions were placed in the inner vessels, which were surrounded by 25ml of  $0.5 \pm 0.1\%$  mercaptan in DMF solutions in the outer “jacket” chamber. Controls consisting of “jackets” containing DMF only were also included. Again, sampling and measurements were taken as previously described in Chapter 4.

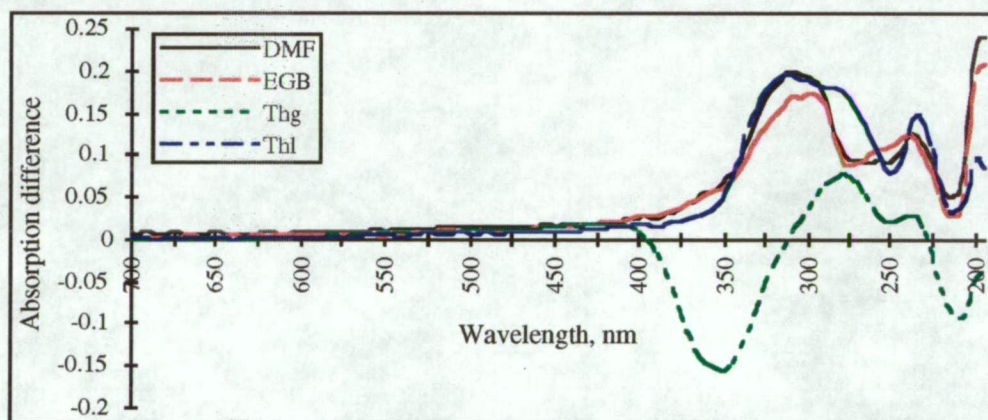


### 6.3.3 Results and Discussion

#### a. Testing for a shielding, or UV-absorption, mechanism of reversion inhibition by mercaptans on MLCs

##### *Guaiacol*

Table 6.9 shows the changes in the absorption coefficients,  $k$ , and tristimulus colour parameters  $L^*$ ,  $a^*$  and  $b^*$  for guaiacol after 12 hours of irradiation while surrounded by the “jacket” solutions. A summary of the changes in these parameters obtained from Chapter 5, in which similar solutions were irradiated but in contact with the mercaptan solutions, has also been included in this table for easy comparison. UV-visible absorption difference spectra showing the spectral changes in the guaiacol solutions after 12 hours of irradiation surrounded by mercaptan “jackets” are shown in Figure 6.23. The equivalent absorption difference spectra for guaiacol treated *with* mercaptans (i.e. in contact with the mercaptans) and irradiated for 12 hours were discussed in Chapter 5, and shown in Figure 5.2b. Comparisons will be made with this figure where indicated.



**Figure 6.23.** UV-visible absorption difference spectra (12-0 hours) for guaiacol surrounded by mercaptan “jackets” and irradiated for 12 hours by Ultravitalux sunlamps.

In Chapter 5, the photo-induced reversion of guaiacol was completely inhibited by each mercaptan. This was supported both by the lack of changes for the mercaptan treated samples in the colour parameters (reproduced in Table 6.9), and the lack of increased absorption above 300nm (“yellowing” peaks), which was seen in the untreated control’s UV-visible absorption difference spectra (see Chapter 5, Figure 5.2b). On applying the mercaptans externally as a “jacket”, however, no inhibition was observed by either mercaptans, which was indicated by each of the colour parameters and the absorption coefficient changes shown in Table 6.9, tending towards darkening and yellowing.

**Table 6.9.** Changes in the absorption coefficients,  $k$  ( $\text{g/m}^2$ )<sup>-1</sup>, and tristimulus colour parameters  $L^*$ ,  $a^*$  and  $b^*$  after 12 hours of irradiation by Ultravitalux sunlamps (12 - 0 hours) for guaiacol irradiated in the direct presence of mercaptans (taken from Chapter 5) or surrounded by “jackets” containing mercaptan solutions.

Mercaptan	$\Delta k^a$	$\Delta L^*$	$\Delta a^{*a}$	$\Delta b^{*a}$
In direct contact with mercaptans (from Chapter 5)				
DMF	0.8	-0.41±0.03	0.3	0.9
EGB	-0.1	0.01±0.03	0.0	0.0
Thg	0.0	-0.03±0.03	0.0	0.1
Thl	0.1	0.19±0.03	-0.1	0.4
Surrounded by a “jacket” containing mercaptans				
DMF	1.6	-0.79±0.04	0.6	1.1
EGB	1.3	-0.70±0.04	0.5	1.2
Thg	2.8	-1.1±0.04	0.7	1.8
Thl	1.4	-0.64±0.03	0.4	0.9

<sup>a</sup>Note that the standard deviations are ±0.1 unless stated otherwise.

For the “jacket” experiment, the “yellowing” peaks seen in the absorption difference spectrum for the DMF control were also formed for the samples surrounded by EGB or Thl “jackets” on irradiation (Figure 6.23), confirming that no inhibition of reversion had occurred. Thus, it appears that for inhibition of the photo-induced discolouration of guaiacol by EGB or Thl, contact is required between guaiacol and the mercaptan.

The UV-visible absorption spectra for the Thg samples revealed a different response than those observed for Thl and EGB, both in Chapter 5 and in the current “jacket” experiment. The spectra for Thg in Chapter 5 and the current experiment were, however, similar to each other, except that the “jacket” spectrum had undergone a small bathochromic shift in all peaks. A large decrease in absorption which was observed at 340-350nm would support a removal of discolouration, and therefore an inhibition of reversion for both the Thg “jacketed” sample, and its analogous sample from Chapter 5. This was not supported by the colour parameters for the “jacket” experiment, however, with the Thg “jacket” appearing to have increased the colour formation, not removed it. A slight increase in absorption above 400nm for the Thg “jacketed” sample, which was not observed in Chapter 5, could account for this. It could be that Thg does not interact directly with guaiacol while inhibiting its reversion, as the UV-visible absorption difference curves were similar both in its direct and indirect presence. It could act by removing coloured products (absorbing

beyond 400nm) of irradiated guaiacol, though, as they form. For Thg acting on guaiacol such a “removal” mechanism was indeed a strong possibility in Section 6.1.

### Vanillin

Table 6.10 shows the changes in the absorption coefficients,  $k$ , and tristimulus colour parameters  $L^*$ ,  $a^*$  and  $b^*$  for vanillin after 12 hours of irradiation while surrounded by the “jacket” solutions. A summary of the changes in these parameters obtained from Chapter 5, in which similar solutions were irradiated but in contact with the mercaptan solutions, has also been included in this table for easy comparison. UV-visible absorption difference spectra showing the spectral changes in the MLC solutions after 12 hours of irradiation surrounded by mercaptan “jackets” are shown in Figure 6.24. The equivalent absorption difference spectra for vanillin treated *with* mercaptans and irradiated for 12 hours were discussed in Chapter 5, and shown in Figure 5.6b. Comparisons will be made with this figure where indicated.

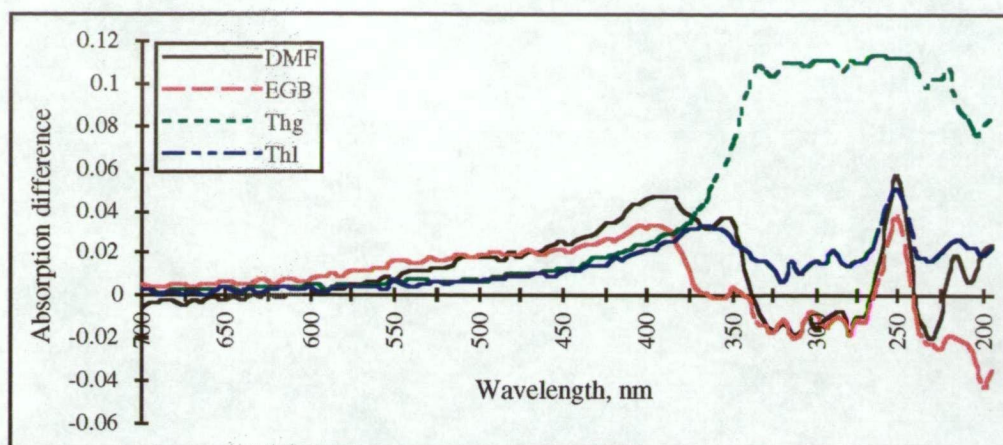
Unlike guaiacol discussed above, vanillin did display successful, albeit partial, inhibition by all three mercaptans via the “jacket” application. This was shown by lesser changes in the colour parameters in Table 6.10, compared to the control surrounded by only a DMF “jacket”. A greater efficiency was even apparent for Thg and Thl “jackets” over their direct applications taken from Chapter 5, which also revealed only a partial inhibition by each mercaptan.

**Table 6.10.** Changes in the absorption coefficients,  $k$  ( $\text{g/m}^2$ )<sup>-1</sup>, and tristimulus colour parameters  $L^*$ ,  $a^*$  and  $b^*$  after 12 hours of irradiation by Ultravitalux sunlamps (12 - 0 hours) for vanillin irradiated in the direct presence of mercaptans (taken from Chapter 5) or surrounded by “jackets” containing mercaptan solutions.

Mercaptan	$\Delta k^a$	$\Delta L^*$	$\Delta a^*$	$\Delta b^*$
In direct contact with mercaptans (from Chapter 5)				
DMF	5.2±0.4	-1.2±0.1	-0.1	3.2±0.4
EGB	2.6	-0.71±0.03	-0.3	3.0
Thg	2.5	-0.78±0.03	-0.4	3.1
Thl	2.6	-0.69±0.03	-0.1	3.2
Surrounded by a “jacket” containing mercaptans				
DMF	4.1	-1.54±0.03	1.0	2.3
EGB	2.8	-1.35±0.03	1.2	1.5
Thg	1.4	-0.44±0.03	0.0	1.3
Thl	1.0	-0.34±0.03	0.0	1.0

<sup>a</sup>Note that the standard deviations are ±0.1 unless stated otherwise.





**Figure 6.24.** UV-visible absorption difference spectra (12-0 hours) for vanillin surrounded by mercaptan “jackets” and irradiated for 12 hours by Ultravitalux sunlamps.

For the Chapter 5 results, the UV-visible absorption difference spectra (Figure 5.6b) for irradiated vanillin alone and those for vanillin treated with EGB or Thl and irradiated were similar, except that the increases in absorption were less intense for the latter cases. This suggests that the reversion of the EGB and Thl treated samples followed a similar pathway to that of vanillin alone, with less formation of colour products. It therefore seems possible that, in Chapter 5, EGB and Thl may have imparted a small inhibition effect without directly interacting with vanillin. That is, the possibility of UV-absorption and/or shielding mechanism exists. These observations were duplicated in the “jacket” experiments for Thl and EGB (Figure 6.24). Therefore, EGB and Thl may shield vanillin to a small degree, resulting in a small inhibition.

Again, the Thg treated samples underwent different spectral changes to those of the EGB and Thl treatments, both in Figure 6.24 and in Chapter 5. Once again, these spectral changes for vanillin treated with Thg and irradiated were similar in both the direct application (Chapter 5) and the “jacket” application (Figure 6.24). Therefore, it is possible that the inhibition observed for Thg treated vanillin, was also independent of contact between the mercaptan and vanillin.

In addition to the above observations, both Thg and Thl when applied as external “jackets”, revealed an absence of a shoulder at 390nm in their difference spectra (which had appeared in the difference spectra from Chapter 5 for each case), while this shoulder was still present for the EGB “jacket”. This could account for the improved inhibition observed by the colour parameters in Table 6.6, for Thg and Thl acting externally on vanillin. Perhaps Thg and Thl were less efficient UV absorbers or shielders in solution with vanillin, as more competition for UV may have occurred.

## Methoxyhydroquinone

Table 6.11 shows the changes in the absorption coefficients,  $k$ , and tristimulus colour parameters  $L^*$ ,  $a^*$  and  $b^*$  for methoxyhydroquinone after 12 hours of irradiation while surrounded by the “jacket” solutions. A summary of the changes in these parameters obtained from Chapter 5, in which similar solutions were irradiated but in contact with the mercaptan solutions, has also been included in this table for easy comparison. UV-visible absorption difference spectra showing the spectral changes in the MLC solutions after 12 hours of irradiation surrounded by mercaptan “jackets” are shown in Figure 6.25. The equivalent absorption difference spectra for guaiacol treated *with* mercaptans and irradiated for 12 hours were discussed in Chapter 5, and shown in Figure 5.10b. Comparisons will be made with this figure where indicated.

**Table 6.11.** Changes in the absorption coefficients,  $k$  ( $\text{g/m}^2$ )<sup>-1</sup>, and tristimulus colour parameters  $L^*$ ,  $a^*$  and  $b^*$  after 12 hours of irradiation by Ultravitalux sunlamps (12 - 0 hours) for methoxyhydroquinone irradiated in the direct presence of mercaptans (taken from Chapter 5) or surrounded by “jackets” containing mercaptan solutions.

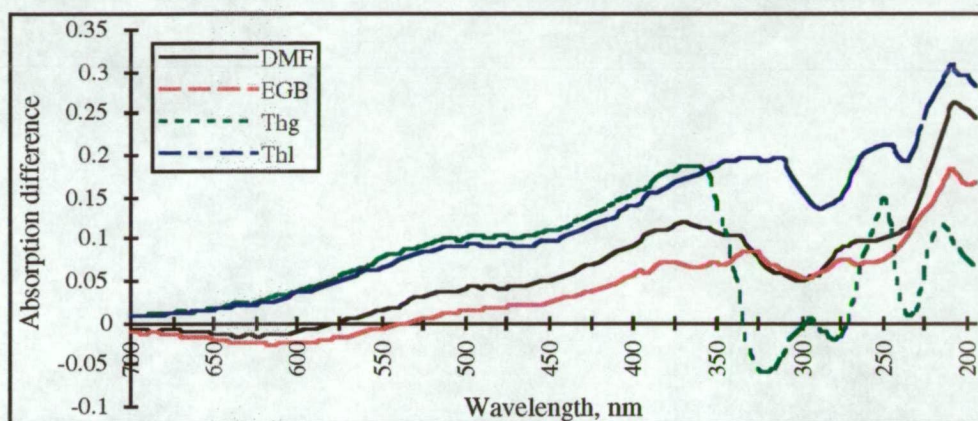
Mercaptan	$\Delta k^a$	$\Delta L^*$	$\Delta a^{*a}$	$\Delta b^{*a}$
In direct contact with mercaptans (from Chapter 5)				
DMF	11.9±0.8	-2.70±0.06	2.3	1.5
EGB	0.7	-0.05±0.03	-0.2	0.8
Thg	1.1±0.2	0.15±0.03	0.0	0.7
Thl	19.2±0.6	-5.16±0.04	4.0	2.9
Surrounded by a “jacket” containing mercaptans				
DMF	33.2±12.1	-2.51±0.07	3.2	5.3
EGB	15.6±5.1	-1.43±0.11	2.3	3.8
Thg	40.6±4.6	-8.14±0.05	5.1	3.5
Thl	46.4±16.7	-8.1±0.19	5.0	3.0

<sup>a</sup>Note that the standard deviations are ±0.1 unless stated otherwise.

For methoxyhydroquinone, enhanced changes in the colour parameters on irradiation (see Table 6.11) revealed that a more intense reversion occurred in the “jacket” apparatus than did in Chapter 5. This was supported by the UV-visible absorption difference spectra in Figures 5.10b and 6.25, with the DMF “jacket” control producing much more intense “yellow” peaks than its counterpart from Chapter 5. These changes were in identical spectral regions, but a broad “quinone” peak at around 525nm did not increase upon irradiation in Chapter 5, while it did increase in the “jacket” experiment. The lack of increased absorption in this region in Chapter 5 was attributed to the original sample already containing quinone species in an



equilibrium, thereby possibly clouding observations of their photo-induced production. This does not explain why the results were not similarly clouded in the “jacket” experiment. Although measurements of the temperature of the inner reaction vessel had revealed that the temperature did not rise significantly, the temperature could not be monitored continuously. It could be that at certain times during irradiation, the temperature of the inner vessel may have increased, and photo-oxidation of methoxyhydroquinone may have been accelerated.



**Figure 6.25.** UV-visible absorption difference spectra (12-0 hours) for methoxyhydroquinone surrounded by mercaptan “jackets” and irradiated for 12 hours by Ultravitalux sunlamps.

Changes in the colour parameters in Table 6.11 revealed that the EGB “jacket” was able to inhibit this reversion, but not as efficiently as the direct EGB application had done in Chapter 5. Thus, although EGB may shield to a degree, the results suggest a stronger inhibition exists which requires contact between EGB and methoxyhydroquinone. The direct application of Thg in Chapter 5 had also resulted in significant reversion inhibition, with little changes in both the colour parameters (Table 6.11) and UV-visible absorption spectra (Figure 5.10b). External application of this mercaptan in the “jacket” experiment, however, revealed no inhibition. In fact, an enhanced reversion of methoxyhydroquinone was indicated by the colour parameters in Table 6.6, along with an increase in absorption beyond 350nm (i.e. increased yellow product formation) against the untreated control’s UV-visible absorption difference spectra (Figure 6.25).

It was proposed in Chapter 5 that the inhibition ability of Thg and EGB could have been due mainly to initial bleaching reactions with methoxyhydroquinone, removing quinone species irreversibly and thus preventing their reformation. The Thg “jackets” failure to inhibit any reversion supports this theory. This mercaptan does not exhibit shielding properties for reversion of methoxyhydroquinone, and direct contact between this mercaptan and methoxyhydroquinone is required to provide the

good inhibition that was observed in Chapter 5. EGB had inhibited slightly more efficiently than Thg in Chapter 5, and this was previously thought to be due to better initial bleaching of the MLC. The UV-visible absorption difference spectra in Chapter 5 revealed little significant changes for the EGB treated sample, which included a lack of formation of quinone (or dimer) species absorbing at 525nm. This supports the irreversible removal of such compounds during bleaching. In the “jacket” experiment this quinone peak did form, but the increase in absorption in this area was to a lesser degree than for the control. This contrasts with the results for the Thg “jacket”. The shape of the EGB “jacket” curve was still similar to the control, however, so it appears that reversion was not prevented, but rather a less intense product formation resulted. Therefore, a small degree of shielding appeared to occur for EGB acting on methoxyhydroquinone, and this may explain the slightly superior inhibition ability of EGB over Thg, which was revealed in Chapter 5.

The Thl “jacket”, like the Thg “jacket” discussed above, also resulted in increased reversion, but for Thl this was also the case for its direct application in Chapter 5. Evidence for this is found in the colour parameter changes in Table 6.6, and also in the UV-visible absorption difference spectra for Thl applied both directly in Chapter 5, and externally in the “jacket” apparatus (Figures 5.10b and 6.25, respectively). Increases in all peak formation (including the quinone peak at 525nm) exceeded those of the untreated controls. The shapes of the spectra are the same in both experiments, so it is possible that the negative effect of Thl on the photo-induced reversion of methoxyhydroquinone is independent of direct contact.

#### **b. Testing for heat interference**

Table 6.12 shows the changes in the colour parameters for the three mercaptan solutions either irradiated with cooling devices (from Chapter 5), irradiated without cooling devices and therefore with possible heat interference, and simply heated for 12 hours. Included in this table are the results for the solvent (DMF) alone. The UV-visible absorption difference spectra for each treatment on the solvent control are shown in Figure 6.26a, and the spectra for the three mercaptans are shown in Figures 6.26b-d. The mass spectra for the mercaptans after each of these treatments are shown in Appendix B.

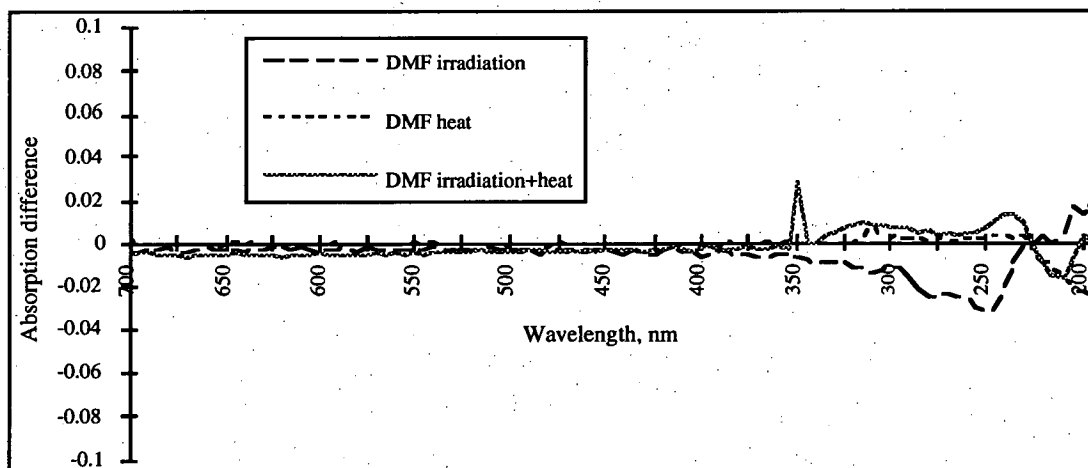
In the irradiation experiments from Chapter 5, all solutions appeared colourless both before and after irradiations. Irradiation in the “jacket” apparatus, with the loss of the cooling device (cold finger), however, may have resulted in a slight discolouration for EGB and Thg, and a definite, if slight, yellow colour formation was observed for Thl. This colour formation was also observed on heating for Thl, but the other two mercaptans appeared colourless after heat treatment.

**Table 6.12.** Changes in the absorption coefficients,  $k$  ( $\text{g/m}^2$ )<sup>-1</sup>, and tristimulus colour parameters  $L^*$ ,  $a^*$  and  $b^*$  after 12 hours (i.e. 12-0 hours) of irradiation by Ultravitalux sunlamps, irradiation with possible heat interference and heating of mercaptan in DMF solutions.

Mercaptan	$\Delta k^a$	$\Delta L^*$	$\Delta a^*a$	$\Delta b^*a$
Irradiation with controlled heat (from Chapter 5)				
DMF	0.0	$-0.01 \pm 0.03$	0.0	0.0
EGB	-0.1	$0.15 \pm 0.03$	0.0	-0.1
Thg	0.1	$-0.02 \pm 0.03$	0.0	0.3
Thl	0.0	$-0.01 \pm 0.03$	0.0	0.2
Irradiation minus heat control ("jacket" experiment)				
DMF	0.1	$-0.02 \pm 0.06$	0.0	0.0
EGB	0.0	$0.08 \pm 0.04$	0.0	0.2
Thg	0.4	$-0.01 \pm 0.03$	0.0	0.5
Thl	$0.8 \pm 0.2$	$-0.16 \pm 0.04$	-0.1	$1.0 \pm 0.2$
Heated				
DMF	0.1	$-0.05 \pm 0.03$	0.0	0.0
EGB	0.0	$-0.01 \pm 0.03$	0.0	0.1
Thg	0.1	$-0.07 \pm 0.03$	0.0	0.3
Thl	0.6	$-0.17 \pm 0.04$	0.0	0.6

<sup>a</sup>Note that the standard deviations are  $\pm 0.1$  unless stated otherwise.

### Solvent control

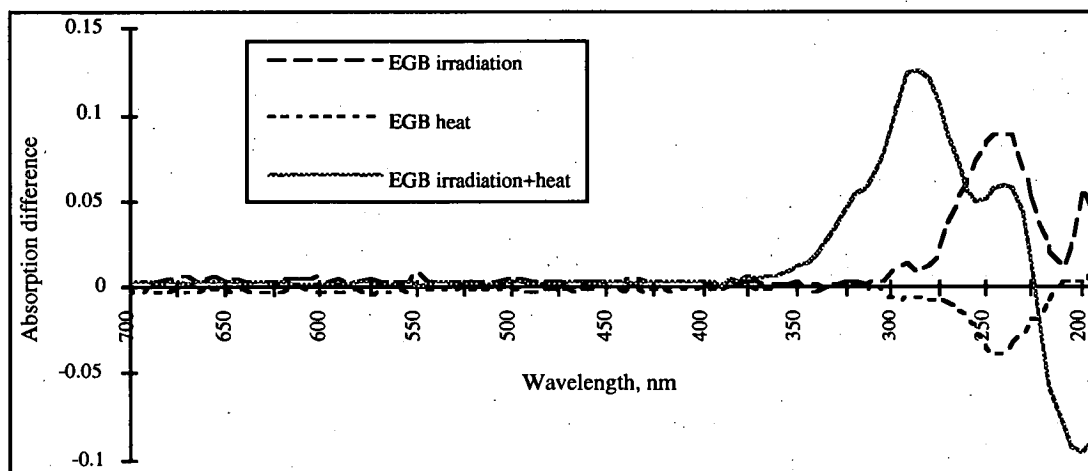


**Figure 6.26a.** UV-visible absorption difference spectra (12-0 hours) for the solvent DMF subjected to irradiation, heating, and irradiation with possible heat interference.



For the solvent control (DMF), no changes were observed for all the colour parameters shown in Table 6.12, and no significant changes in the UV-visible absorption spectra (Figure 6.26a) were observed for each treatment. This confirms the non-reactivity of the solvent to irradiation and/or heat exposure.

### EGB



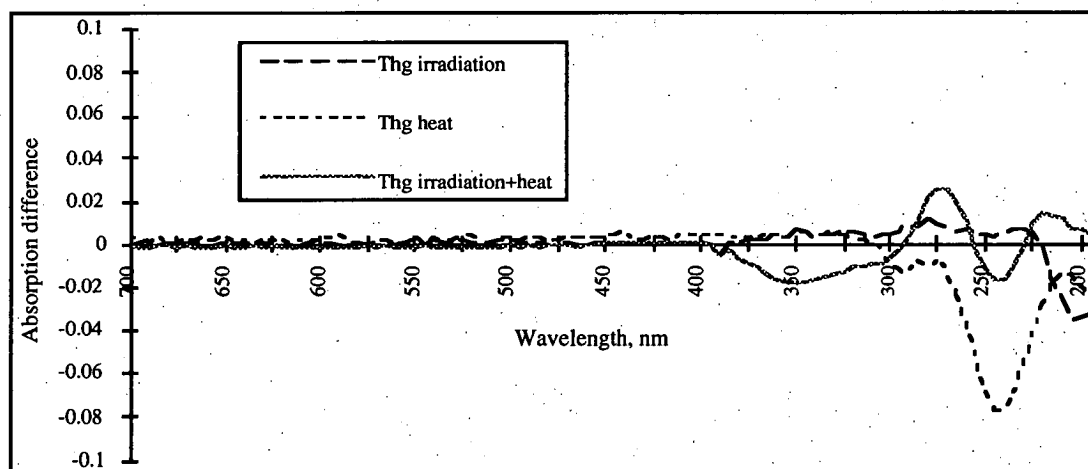
**Figure 6.26b.** UV-visible absorption difference spectra (12-0 hours) for the EGB subjected to irradiation, heating, and irradiation with possible heat interference.

The colour parameters for EGB shown in Table 6.12 revealed that insignificant colour changes had occurred after each treatment. The UV-visible absorption difference spectra (Figure 6.26b) showed that heat caused only a small change (less than 0.05 units) in the absorption of EGB, which was a slight decrease in absorption at 240-245nm. Despite this, when combined with irradiation (i.e. in the “jacket” apparatus), the spectral differences were significantly altered compared to those for irradiation with the cooling devices in Chapter 5. In both irradiation cases, increases in absorption were observed around 285, 240 and possibly 195nm. The latter, though, is close to the lower spectral limit of the spectrophotometer and therefore its peak formation is incomplete and subject to larger error fluctuations.

In Chapter 5 the possibility of EGB experiencing light-induced reactivity about the C=O groups (which absorb at 195nm and 270-285nm), and/or the formation of disulphide bonds (which absorb at 195nm 255nm) was introduced. For the irradiated spectra from Chapter 5, the peak at 240nm is broad, encompassing the region around 255nm. It is therefore possible that the three peaks at 285, 240 and 195nm could indeed support an excited C=O photo-initiated formation of disulphide bonds as shown in Chapter 5, Reaction 3. The difference spectrum for the “jacket” sample revealed similar peaks to the irradiated sample, except the C=O absorbing region at

285nm had increased to a much greater intensity in the presence of heat and light, and a shouldering absorption peak at 320nm had become apparent. This 320nm shoulder was not observed in the irradiated sample from Chapter 5, but could still have been present to a small degree and masked by noise. The three spectra do not indicate that heat has resulted in any significant reaction, but rather it has possibly enhanced the photo-reactions of EGB, particularly the reactivity around the C=O group. The mass spectra of these three treatments of EGB, shown in Appendix B, were identical, confirming that no reaction products, other than those observed for irradiation alone, were formed by heat either alone or combined with irradiation. Thus, if heat had interfered with the ability of EGB to inhibit via a shielding mechanism in the “jacket” experiment, it is likely that it had simply resulted in a more rapid light-induced depletion of EGB.

### Thg



**Figure 6.26c.** UV-visible absorption difference spectra (12-0 hours) for the Thg subjected to irradiation, heating, and irradiation with possible heat interference.

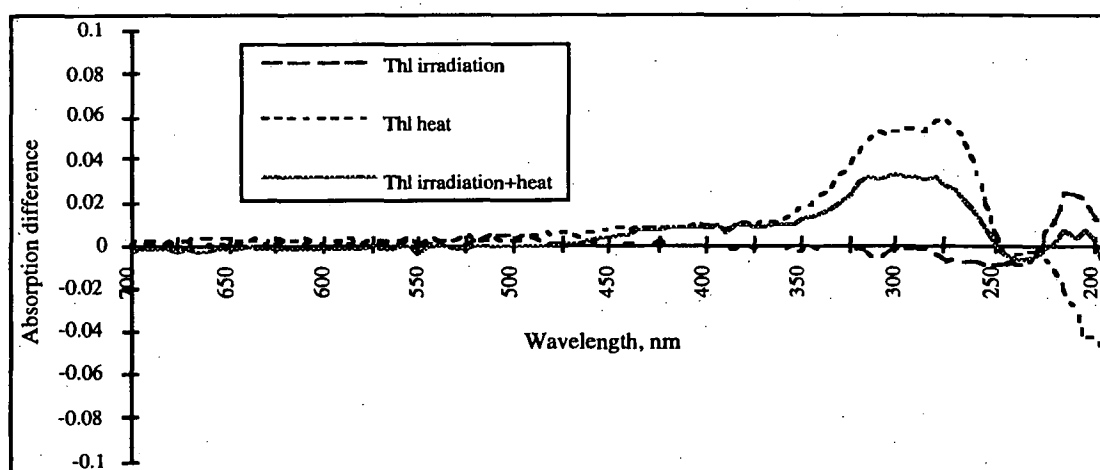
The changes in the colour parameters for Thg presented in Table 6.12 indicate that no significant changes occurred for both the irradiated sample from Chapter 5, and the heated sample. The combination of irradiation and heat in the “jacket” experiment, however, may have caused a slightly greater yellowing, as revealed by a small increase in  $k$  and  $b^*$ . This change was very close to the error limits, and so is for consideration only.

Irradiation alone resulted in little change in the UV-visible absorption difference spectra for Thg (Figure 6.26c). Heating resulted in a decrease in absorption at 240-245nm, a very small decrease at 290nm, and possibly small increases in absorption at 210 and 275-280nm. When heat and irradiation were combined a similar spectra was

obtained, but the increases in absorption at 275 and 210-220nm were more enhanced. Once again this indicates that heat could have increased the photo-activity of the C=O groups, but the effects of the heat spectrum were also evident in the combined irradiation with heat spectrum. This contrasts with the results for EGB above. Therefore, in this case it is possible that heat had indeed a significant independent effect on Thg, and may have altered its light-induced reactions. Unfortunately, the heat experiments were not excluded completely from laboratory lighting, so some uncertainty exists. It could be that the heat-induced changes (other than the decrease in absorption at 240nm, which was not observed for the irradiated samples) could have been due to residual light entering the experiment.

The mass spectra, shown in Appendix B, revealed no differences between all three treatments of the Thg samples, but an increase in photo-induced dimer products was apparent in the presence of heat. Therefore, for Thg it is possible (but not certain) that heat has independently affected the mercaptan, while also increasing its photo-activity.

### Thl



**Figure 6.26d.** UV-visible absorption difference spectra (12-0 hours) for the Thl subjected to irradiation, heating, and irradiation with possible heat interference.

Although the mass spectra (see Appendix B) did not reveal any significant differences between Thl for each treatment, it still appears that heat had a distinct effect on this mercaptan. Thl underwent yellowing by both the heat treatment and irradiation in the “jacket” apparatus, indicated by similar increases in both  $b^*$  and the absorption coefficient,  $k$ , along with a small darkening indicated by a decrease in  $L^*$ , shown in Table 6.12 above. For irradiation alone in Chapter 5, none of these changes were observed. The UV-visible absorption difference spectra (Figure 6.26d)

for irradiation alone revealed no significant changes, but the spectra for both heat alone, and heat in conjunction with irradiation, revealed similar changes with respect to each other. Increased absorption occurred at 210nm, and also more markedly between 270 and 315nm. This latter absorption tailed into the lower visible region, and this could account for the observed yellow colouration. The changes in absorption were more intense for the heated sample. Therefore, it is likely that the spectral changes in Thl tests were a result of the heat rather than an increased photo-activity due to heat, as (unlike Thg and even more unlike EGB), these changes were not observed even to a small degree for the irradiated sample from Chapter 5. Thus it is probable that heat has definitely caused an independent reaction in Thl, and therefore possibly interfered with its photo-reactions and/or inhibition potential.

### *In summary*

Heat could have affected all three mercaptans, EGB to a marginal degree, Thg to a small degree, and significantly for Thl. Enhancement of photo-reactions seems to be the principal effect of heat interference for EGB, and perhaps to a smaller degree for Thg, but the effect on Thl seems to be independent of irradiation. Despite these findings, some shielding from light was observed in all mercaptans, including Thl, when surrounding vanillin in the "jacket" apparatus (discussed above). So, the heat interferences do not appear to have destroyed the shielding abilities of these mercaptans. For Thl in particular, though, the possibility of heat interference must still be considered.

### **6.3.4 Conclusions**

- As for previous discussions on the reversion inhibition abilities of mercaptans, results obtained were not universal. Prior to summarising this, it should be noted that heat complications may have distorted the results of shielding for Thl, and possibly to a small degree for Thg and EGB "jackets".
- Despite the possible heat interference, all three mercaptans studied exhibited shielding ability in the reversion of vanillin. This shielding effect was comparable to the inhibition observed when the mercaptans and vanillin were in contact (Chapter 5), so it is possible that shielding is the major, if not only, mode of inhibition of the photo-induced reversion of vanillin.

- Conversely, the results of guaiacol studies revealed no evidence of shielding ability for any of the three mercaptans. In light of the excellent inhibition observed for each mercaptan acting on guaiacol from Chapter 5, it can be concluded that contact is required between the mercaptan and guaiacol for inhibition to occur.
- For methoxyhydroquinone, Thl exerted no positive inhibition either when in contact with the MLC (Chapter 5) or while acting as a shield (in the “jacket”). Although Thg was found to exhibit no shielding, it provided excellent inhibition ability while in contact with methoxyhydroquinone. Thus, for Thg acting on methoxyhydroquinone, contact is required for inhibition to be effective, and this could possibly be due to an initial irreversible bleaching by this mercaptan. This was also found to be the case for EGB acting on methoxyhydroquinone, possibly being its major mode of inhibition. EGB also exhibited a minor shielding, providing evidence of a possible dual inhibition mechanism for EGB. These results are summarised in the table below:

MLC	“shielding” possible	“shielding” unlikely
guaiacol	-	EGB, Thg, Thl
vanillin	EGB, Thg, Thl	-
methoxyhydroquinone	EGB	Thg, Thl

Therefore, while each mercaptan was found to exhibit a shielding mechanism, whether or not this is an effective mode of photo-reversion inhibition is highly dependent on the yellowing species it is acting on.



## CONCLUSION

The results presented in this thesis have confirmed that mercaptans inhibit the photo-induced reversion of lignin-rich pulps and model lignin compounds. This inhibition was shown to vary in both its effectiveness and its mechanism, depending on the mercaptan used and the species it is acting on. Several modes of inhibition were investigated, and each was found to occur (or be possible) for mercaptans acting on MLCs. The general finding was that no mercaptan universally inhibited all the MLCs studied, and no MLC was universally inhibited by all the mercaptans studied.

A sequence of investigations were needed in order to arrive at this conclusion. Firstly, photo-reversion had to be artificially simulated. Following this, the ability of mercaptans to inhibit needed to be confirmed. Once this was confirmed, mechanistic studies could commence. For such studies, a knowledge of what kind of compounds actually photo-yellow, and which of these actually undergo inhibition by mercaptans, was required. With this knowledge, mechanistic studies could then commence on appropriate MLCs. The findings from each step in this investigation will be summarised below, ending with the conclusions of the mechanistic studies.

### 1. Artificially simulating reversion.

In Chapter 2, it was determined that Ultravitalux sunlamps simulated natural sunlight-induced reversion extremely well. They were shown to cause similar colour changes and induce similar chemical changes to those induced by the sun, both in TMP and peroxide bleached TMP (BTMP) handsheets. This can be attributed to the spectral energy distribution of these sunlamps matching that of sunlight with regards to the relative intensities of spectral regions involved in paper photochemistry. Although these lamps emitted high temperatures, thermal reversion complications were found to be negligible for handsheet studies. For solution studies the attachment of a cooling device to the reaction vessel prevented overheating.

The reversion induced by these lamps involved the formation of coloured quinone species in both TMP and BTMP. Results seemed to indicate that BTMP may have undergone greater reversion than TMP, and this was subsequently verified in Chapter 3. This was attributed to coniferaldehyde species, which had been previously removed by peroxide bleaching, being reformed during the irradiation of BTMP.

## **2. Confirming the ability of mercaptans to inhibit the reversion of lignin-rich pulp.**

In Chapter 3, the ability of mercaptans to inhibit the reversion of TMP and BTMP handsheets was confirmed for three mercaptans; ethylene glycol bithioglycolate (EGB), thioglycolic acid (Thg), and thiolactic acid (Thl). EGB was found to be the strongest, giving almost complete inhibition.

For this inhibition to occur, it was found that the mercaptans were required to remain within the handsheet throughout irradiation. This implied that the mechanism involved a continual process, for example, by shielding chromophoric groups from UV radiation, or by removing or bleaching coloured species as they formed.

Along with inhibition, the bleaching ability of mercaptans was also confirmed in Chapter 3. This bleaching was found to be similar to alkaline peroxide bleaching, in that it involves the removal of coniferaldehyde species. The mechanisms of these two bleaching agents, however, may not be the same. Results suggested that while peroxide bleached handsheets undergo a reformation of coniferaldehyde species during irradiation, EGB bleached handsheets do not. Therefore, peroxide bleached handsheets possibly contain photo-reactive species that are distinct from EGB bleached handsheets.

Bleaching by EGB also appeared to occur in two stages, involving an initial removal of red chromophores, followed by a slower removal of yellow chromophores. At least for the slower bleaching action of EGB on TMP, an equilibrium process may be involved which requires an excess of EGB for the bleaching to be maintained. Removal of this excess EGB (by washing with acetone) may reverse the equilibrium to favour the reformation of previously bleached coloured species. This was suspected, because EGB-treated handsheets which were washed prior to irradiation underwent a greater discolouration than handsheets that had not been treated at all. It appeared that the washed samples had developed two sources of discolouration, one being the photo-induced reversion, and the other being a reformation of previously bleached chromophoric groups. These combined processes resulted in the appearance of an enhanced reversion. For similarly treated BTMP handsheets, such enhanced discolouration was not observed. This is because the initial bleaching by EGB was low (due to peroxide bleaching having already removed many chromophoric groups), and so the reformation of EGB-bleached coloured species was minimal.

### 3. What kind of species undergo photo-reversion?

In Chapter 4, studies on model lignin compounds (MLCs) revealed that for reversion to occur compounds must contain a phenolic hydroxyl group. This does not preclude compounds which lack this group from playing a significant role in photo-yellowing, however, as some such compounds (e.g. benzophenone) appeared to undergo photo-activity without a discolouration effect. Compounds such as this could still play an indirect role in lignin photo-yellowing by behaving as a photo-sensitiser to yellowing reactions.

Side chain C=O or C=C groups (e.g. acetovanillone, eugenol), or ring-substituted COOH or CHO groups (e.g. vanillic acid, vanillin), in conjunction with the phenolic hydroxyl group, may enhance reversion by acting as photo-sensitising groups. Interestingly though, compounds which contained a COOH or CHO end group in *conjugation* with a 3-carbon side chain C=C “photo-sensitising” group (e.g. ferulic acid and 4-hydroxy-3-methoxy cinnamaldehyde) did not photo-revert. These end groups appeared to interfere with the sensitisation step.

Quinone and hydroquinone compounds photo-yellowed efficiently, irrespective of methyl or methoxyl substituents. The unsubstituted quinone and methoxyl-substituted hydroquinone samples established a redox system, and developed some oxidation products under atmospheric conditions, prior to irradiation. The methyl-substituted hydroquinone did not form any oxidation products, nor did it establish a redox system, prior to irradiation.

As to the mechanism of photo-yellowing: most compounds underwent dimerisation upon irradiation, which could have occurred via H-abstraction. Subsequently formed radicals could then have combined (e.g. guaiacol). Most compounds were also found to have probably formed quinone species or intermediates, as well as having undergone cleavages of simple substituted groups (i.e. demethylation and/or demethoxylation) upon irradiation. This latter process could also have resulted in the formation of radicals.

### 4. Which species that undergo reversion are also inhibited by mercaptans?

In Chapter 5, MLCs that had previously photo-reverted in Chapter 4 were shown to undergo a diverse response to inhibition by mercaptans. Three general responses were noted, and they are summarised below.

*i) A complete inhibition of reversion by all mercaptan treatments.*

This was observed for guaiacol, isoeugenol, and vanillic acid. There were no clear structural trends to explain the similar inhibition experienced by each of these MLCs, as they each had different C1 substitutions (guaiacol had no C1 substitution, vanillic acid had a carboxylic acid group at C1, and isoeugenol contained a 3-carbon side chain at the C1 position).

For each of these compounds it appeared that Thg and Thl may have inhibited through similar mechanisms, which were different in turn to those of EGB. Thg and Thl may have inhibited reversion via an initial reaction with the MLC, which arrested reversion at an early stage. This may have involved a removal of the phenolic hydroxyl group of the MLC via reaction with the COOH group of these two thiocarboxylic acids. For EGB, no initial reaction with these MLCs was indicated. This suggested that EGB inhibition possibly involved ongoing processes during irradiation. For example, EGB may shield the MLC from UV radiation, or it may remove coloured products of irradiation as they are formed.

*ii) A partial inhibition, no inhibition or enhanced discolouration by all mercaptan treatments.*

Quinone species, vanillin and syringaldehyde were all shown to undergo a varied response to mercaptan treatment. For example, while Thg and EGB inhibited the reversion of methoxyhydroquinone quite well, Thl actually enhanced its discolouration. Each of the MLCs mentioned here contained a phenolic or aldehyde group substituted at the C1 position.

Except for methylhydroquinone, which was originally colourless, an initial bleaching of these MLCs was also observed for each mercaptan treatment. As inhibition for methoxyhydroquinone was almost complete by EGB and Thg treatments, the initial bleaching by these mercaptans may have occurred via an irreversible process, preventing the re-formation of coloured quinone species.

It was suggested that for methoxyhydroquinone and vanillin, the initial bleaching by the mercaptans was likely to be a reduction of pre-existing quinone species (originally present in both these MLC samples as a result of atmospheric oxidation), and a Michael-type addition of the thiols to these quinones, resulting in the formation of corresponding *p*-hydroquinone compounds that either contained or did not contain a thiol residue. This hydroquinone species could then have undergone photo-oxidation during irradiation, to re-form its corresponding quinone. Subsequent reduction of this quinone species by mercaptans would establish a reduction-

oxidation-reduction cycle. As this cycle proceeds, a gradual depletion of active thiol groups would result in an overall inefficiency in inhibition.

Inhibition of reversion by each mercaptan could still have occurred via this mechanism even if the initial bleaching had not occurred. In such a case, the cycle would be initiated by mercaptan-induced reduction of quinones produced during photo-reversion.

The varied efficiencies of inhibition observed for these MLCs treated with each mercaptan could be explained by different rates of the reactions involved in the above cycle, with each reaction rate being dependent on the different MLC-mercaptan components of each system.

*iii) An introduction of photo-induced yellowing by treatment with each mercaptan.*

Although 3-methoxy-4-hydroxy cinnamaldehyde did not undergo photo-yellowing in Chapter 4, it was still included in the study in Chapter 5. This was because it had exhibited a unique response to irradiation in Chapter 4, in that it *may* have undergone a minor photo-bleaching effect. Its response to mercaptan treatment before irradiation was therefore assessed out of interest. Surprisingly, the presence of each mercaptan *caused* this compound to photo-yellow.

It is possible that the initial bleaching reaction of mercaptans on this MLC was actually responsible for its subsequent reversion. More specifically, it is proposed that the bleaching action of mercaptans on this MLC destroyed its side chain conjugation. In Chapter 4, it was proposed that it was this conjugation that had prevented this MLC from photo-yellowing in the first place.

In addition to this, the presence of Thg and Thl may also have resulted in (or catalysed) the formation of coloured quinone species during irradiation of this MLC, which were not detected in the absence of Thg or Thl. This would also explain the enhanced discolouration, as quinones are strongly coloured.

**5. Finally, what are the mechanisms by which mercaptans inhibit reversion?**

At the onset of this project, it was hoped that the answer to this question would be a simple statement, consisting of a clear and concise *universal* mechanism. This is not possible, however, as the inhibition of reversion by mercaptans is a complex process involving several different inhibition mechanisms, which vary in their effectiveness, and possibly even existence, depending on the species a mercaptan is acting on. For



example, three completely separate mechanisms were investigated in Chapter 6, and the results revealed that each mechanism either occurred or had the potential to occur. The results were erratic, however, with the three mercaptans having different responses, and the same mercaptan having different responses with different MLCs. These results are summarised below:

*a) Mercaptans inhibiting reversion by removing coloured products as they are formed.*

Removal of coloured products of irradiation as they formed was found to be a strong possibility for all mercaptans acting on isoeugenol, as well as EGB acting on methoxyhydroquinone and TMP handsheets, Thg acting on methoxyhydroquinone and acetovanillone, and Thl acting on acetovanillone. Each of these MLC/mercaptan combinations had experienced complete inhibition of reversion, and the mercaptan was able to completely restore these irradiated MLCs to their original colour. Isoeugenol was originally colourless, and therefore the removal of colouration in the irradiated samples by each mercaptan can be attributed to a complete removal of coloured products of irradiation. Thus, for this compound it appears that a "removal mechanism" may be the sole, or at least major, form of inhibition. The remaining MLCs and the TMP handsheets mentioned above were originally coloured and had been previously shown to undergo bleaching by each mercaptan. Therefore the respective mercaptans were able to either completely or at least partially remove coloured products of irradiation for these compounds / handsheets, depending on the extent of simultaneous bleaching of native coloured species.

The potential for mercaptans to remove coloured species as they are formed was also shown for each mercaptan acting on guaiacol and vanillic acid. Results in Chapter 6 revealed that mercaptans were only able to partially restore these irradiated compounds back to their original colourless state. As these compounds were originally colourless, simultaneous bleaching would not have occurred along with removal of coloured products of irradiation. Therefore, each mercaptan was able to remove a portion of the coloured irradiation products. These compounds had, however, been shown to undergo complete inhibition by each mercaptan treatment in Chapter 5. Therefore, it is clear that if a removal mechanism does occur for these MLCs, it does not act alone. That is, more than one mechanism of inhibition is involved for these MLCs.

Other MLCs were shown to contain the potential to remove coloured products as they are formed, but only to a minor extent. BTMP handsheets were shown not to be inhibited in this way.

*b) Inhibiting the photo-sensitisation of MLCs during irradiation.*

Inhibition of photo-sensitisation also varied, depending on both the photo-sensitiser involved and the model lignin compound acted upon. Acetophenone sensitised the photo-reversion of two out of three model lignin compounds (guaiacol and methoxyhydroquinone), and in each case EGB was unable to inhibit this sensitisation. Therefore, for the photo-sensitiser acetophenone, EGB has no ability to interfere with sensitisation. The presence of this photo-sensitiser even destroyed EGB's previously shown inhibition abilities. For methoxyhydroquinone at least this could be due to the sensitiser reducing the ability of EGB to remove coloured species as they form, or its efficiency in doing so.

Acetoveratrone acted as a sensitiser in the photo-reversion of all three model lignin compounds studied (guaiacol, methoxyhydroquinone, and vanillin). EGB was able to inhibit this sensitisation completely for guaiacol, although its previously shown photo-reversion inhibition ability was slightly diminished. For vanillin, a partial inhibition of sensitisation by EGB was revealed. For methoxyhydroquinone, not only was EGB ineffective in inhibiting the sensitisation by acetoveratrone, its previously shown bleaching ability was diminished, while its previously shown inhibition of photo-reversion was completely destroyed by the presence of this photo-sensitiser.

Therefore while mercaptans are able to interfere with photo-sensitisation in some cases, they have a detrimental effect, even increasing sensitisation in others.

*c) Shielding chromophoric groups from UV irradiation.*

Once again, on the reversion inhibition abilities of mercaptans, results obtained were not universal. All three mercaptans studied exhibited the ability to shield vanillin from UV radiation. This shielding effect was comparable to the inhibition observed when the mercaptans and vanillin were in contact, so it is possible that shielding is the major, if not the only mode of inhibition for the photo-induced reversion of vanillin.

Conversely, the results for guaiacol revealed no evidence of effective shielding by each of the three mercaptans. In light of the excellent inhibition observed for each mercaptan acting on guaiacol, it can be concluded that contact is required between the mercaptan and guaiacol for inhibition to occur. This was also the case for Thg acting on methoxyhydroquinone. This reinforces the possibility that inhibition in this case involved an initial irreversible bleaching by this mercaptan. This is probably also the major mode of inhibition for EGB acting on

methoxyhydroquinone. EGB also imparted a minor shielding effect however, providing evidence of a possible dual inhibition mechanism for EGB. Thl did not inhibit reversion of methoxyhydroquinone, either when in contact with the MLC, or while acting as a shield in a "jacket" surrounding the MLC.

For EGB at least, the shielding effect seen for vanillin and methoxyhydroquinone may have been a side-reaction to its own interaction with UV-light. EGB was shown in Chapter 5 to undergo oxidative dimerisation, which was enhanced during irradiation. It was proposed that during irradiation, the C=O groups of EGB absorb UV light, becoming excited and initiating hydrogen abstractions of the thiol hydrogen(s). This would result in the formation of a thio-radical intermediate, which could then combine to form the dimers across disulphide bonds. It could be the initial sensitisation, or UV absorption, by the C=O groups that detract UV radiation from other chromophoric compounds. This reaction sequence would also result in the availability of hydrogen atoms to other radicals formed during irradiation. Thus a hydrogen-donation, or radical quenching system would be established, which would prevent yellowing reactions from being completed.

### Suggestions for Further Research

A larger range of MLC inhibition tests would be of great benefit, in order to pinpoint some trends which could explain the varied observations presented in this thesis. For example, vanillin and syringaldehyde (both being 3-methoxy-4-hydroxy compounds with an aldehyde substitution at the C1 position) may have undergone similar modes of behaviour with respect to both reversion and its inhibition by mercaptans. This was difficult to determine accurately, however, on the basis of a comparison between only two such compounds. The effects of irradiation and inhibition on a *range* of methoxy-hydroxy-aldehyde ring substituted compounds would enable a more accurate conclusion to be drawn.

The results of this thesis also suggested that the presence of C=C-C=O conjugation on 3-carbon side chains of a compound blocked reversion. Upon the addition of mercaptans, this conjugation may be destroyed, *enabling* reversion to occur rather than be inhibited. This conclusion should be verified by studying several other MLCs which contain conjugated side chains.

Many different mercaptans have been studied for their inhibition ability (for examples, see Section 1.3), but the emphasis has usually been on the effect of their sulphur-containing group. A range of mercaptans containing different *secondary functional groups* could also be studied, with a view to determine the involvement of

secondary groups. For example, does the presence of a C=O group in a mercaptan *initiate or sensitise* H-abstraction at the thiol-hydrogen, thereby enhancing the mercaptan's ability to donate hydrogen? Also, does a mercaptan containing a carboxylic acid group exert a *dual* inhibitory action, via reactions at *both* the COOH group and the thiol group? Evidence presented in this thesis suggested as such, with Thg and Thl having possible activity at their labile SH groups, along with possible reactivity of their COOH groups. Further GC-MS analyses should at the very least determine the presence or absence of products of reactions between the COOH group of such thiocarboxylic acids and an MLC.

The inhibition of the reversion of a complex system like lignin by mercaptans is a complex process, involving several different modes of action, possibly in competition with each other as well as with yellowing reactions. Mechanistic studies on simple MLCs can enable different processes to be defined, and lead to a greater understanding of their inhibition ability. It is only when such an understanding is reached that mercaptans could be considered for use as inhibitors outside of the laboratory, or be used to model other (less smelly!) potential inhibitors.

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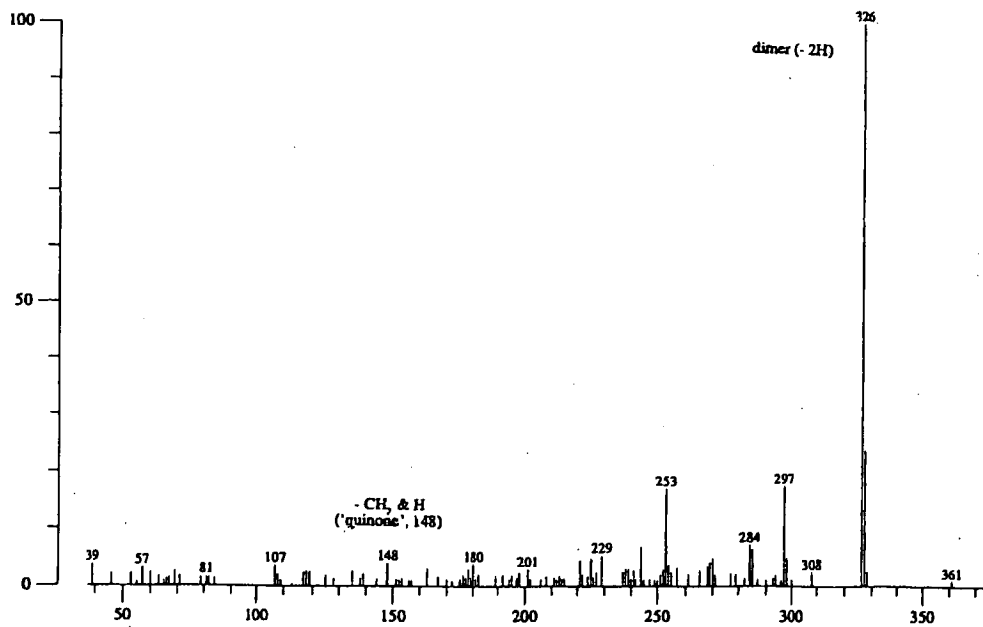
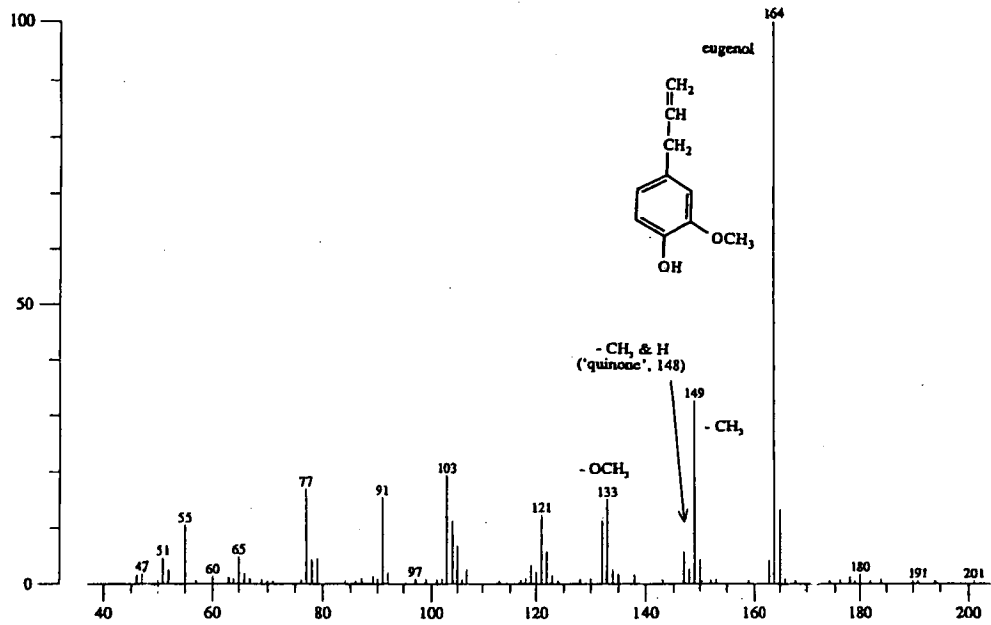


# **APPENDIX A**

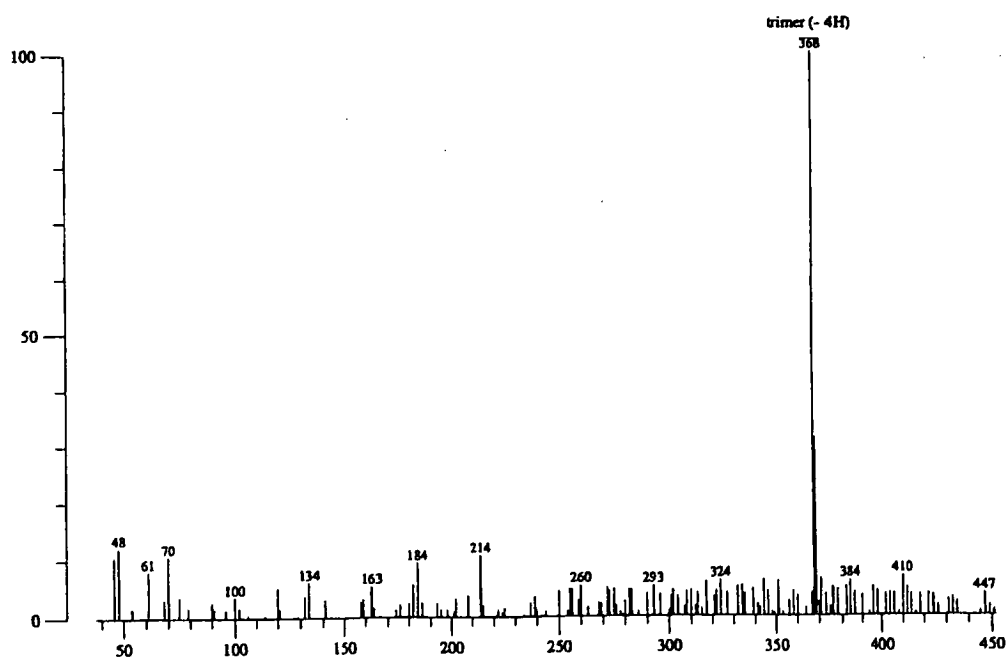
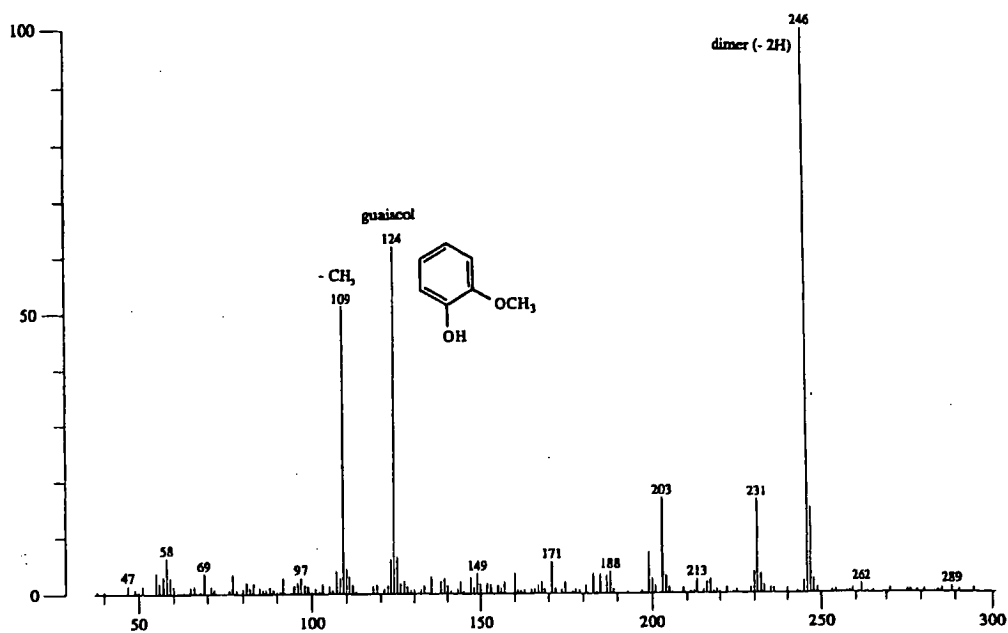
## **Gas Chromatography - Mass Spectra for Irradiated MLCs**

(referenced in Chapter 4)

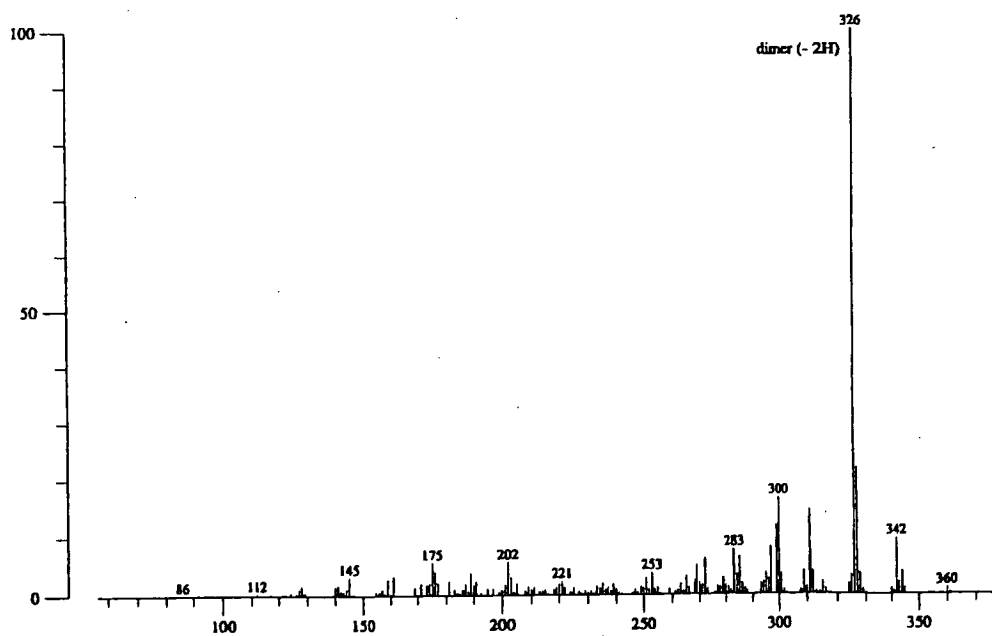
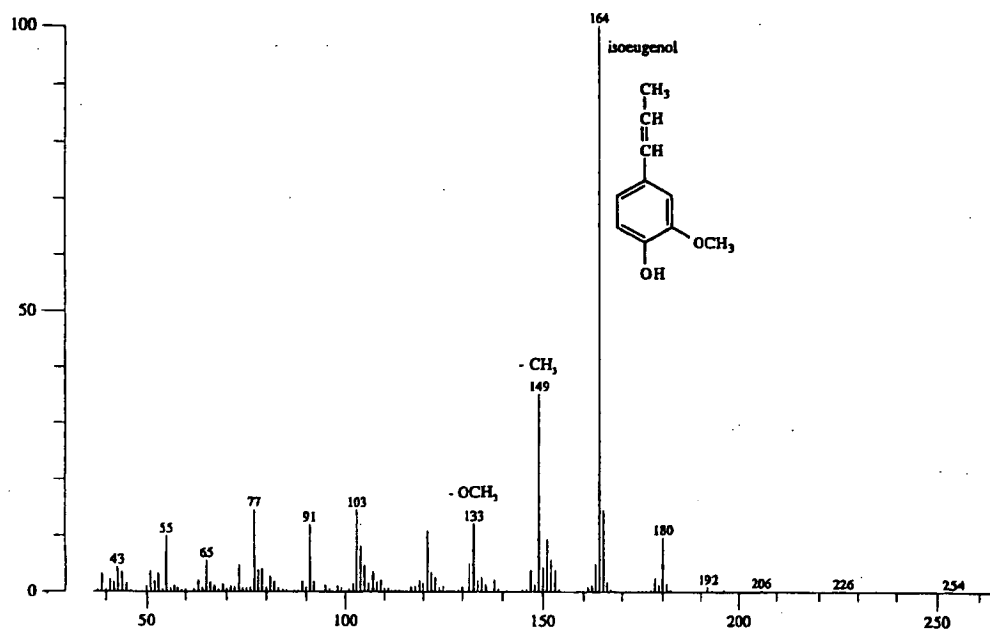
# A1. Gas chromatography - mass spectra for irradiated eugenol.



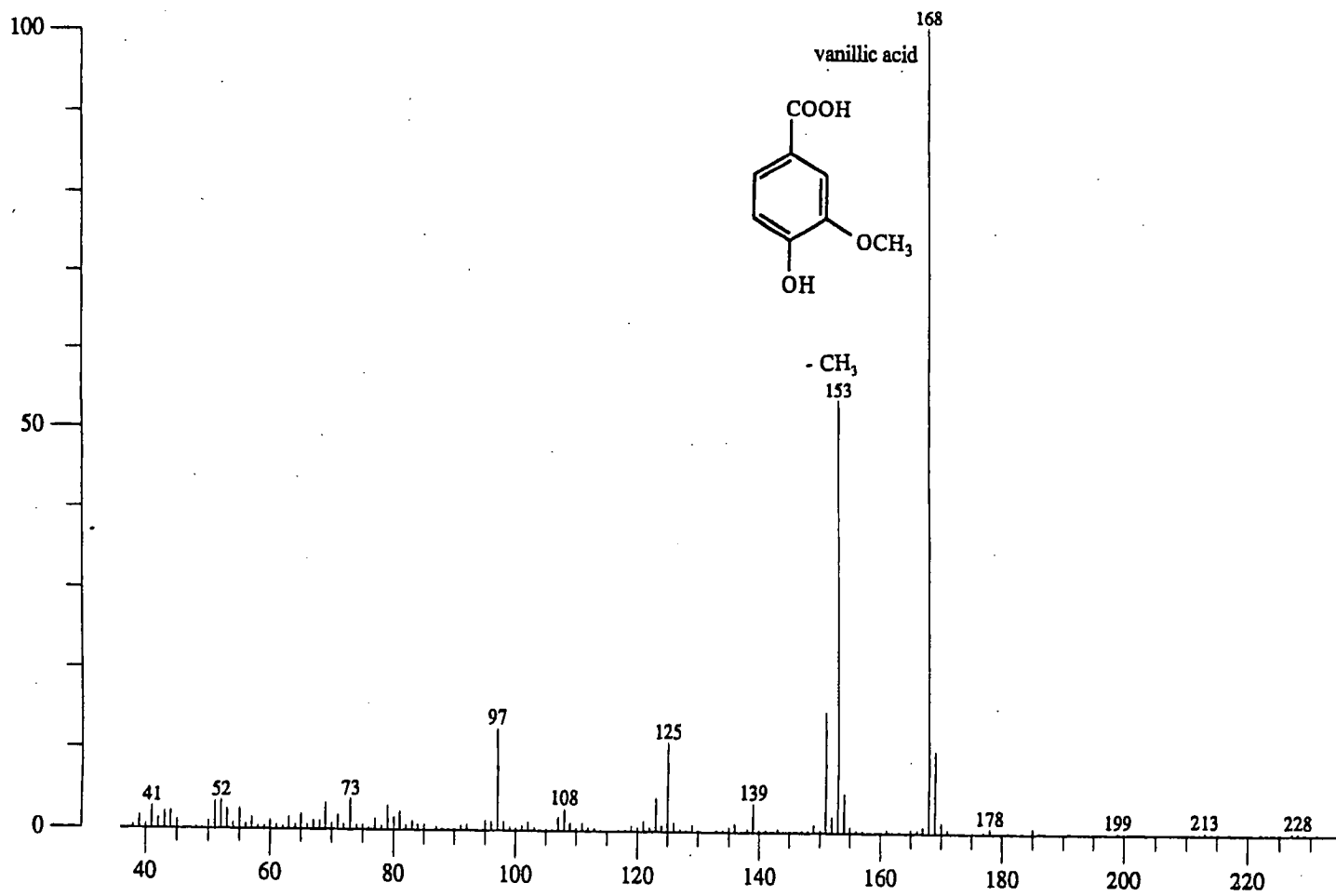
## A2. Gas chromatography - mass spectra for irradiated guaiacol.



### A3. Gas chromatography - mass spectra for irradiated isoeugenol.

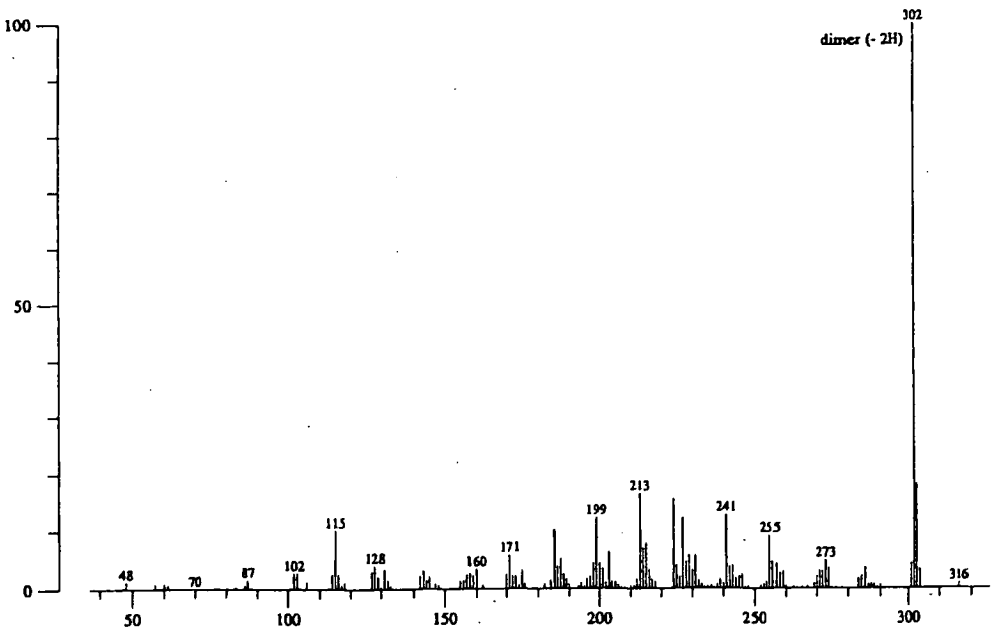
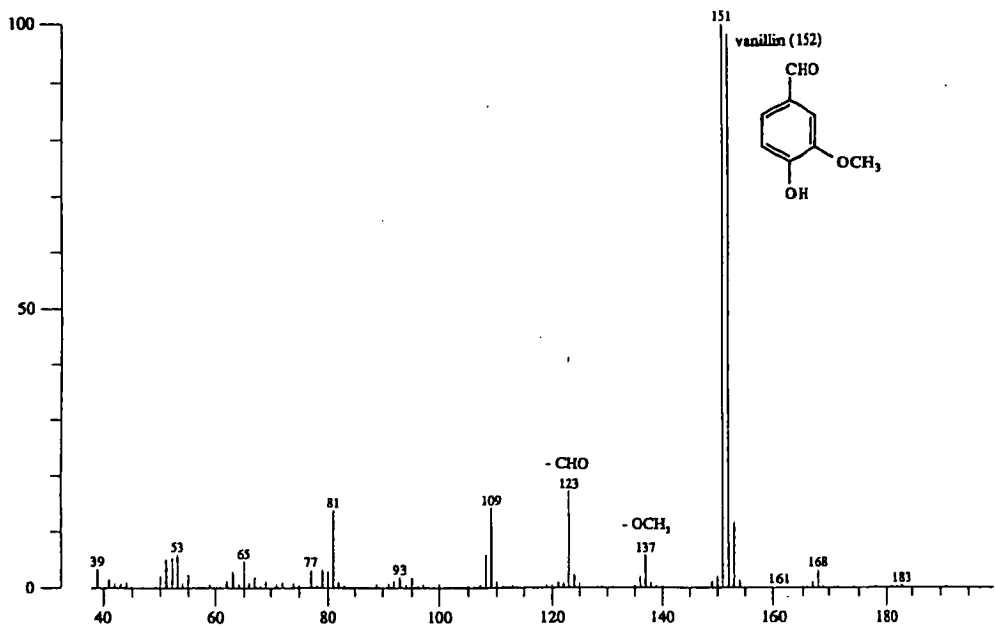


A4. Gas chromatography - mass spectra for irradiated vanillic acid.

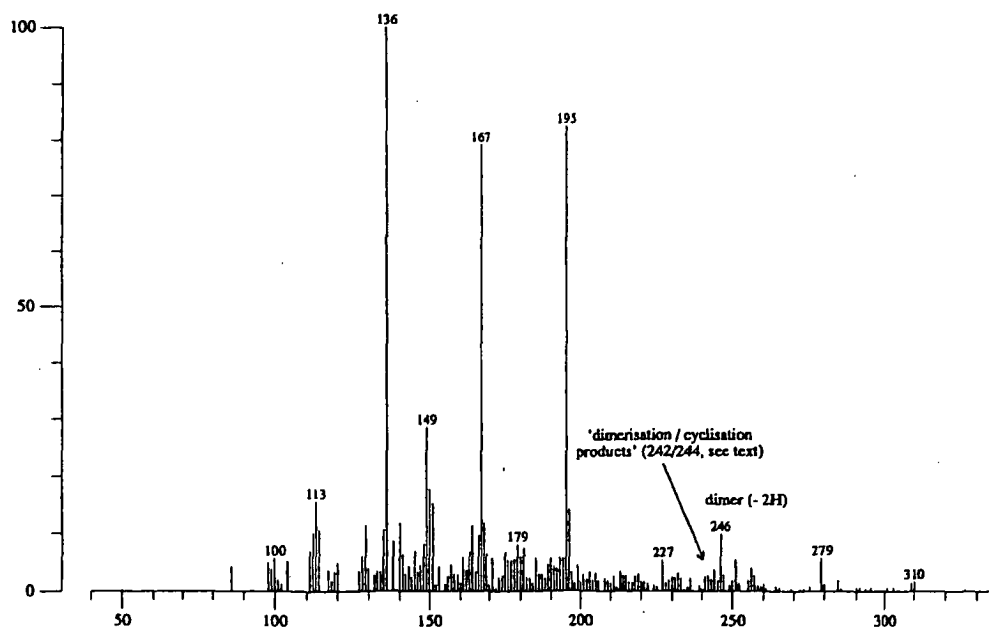
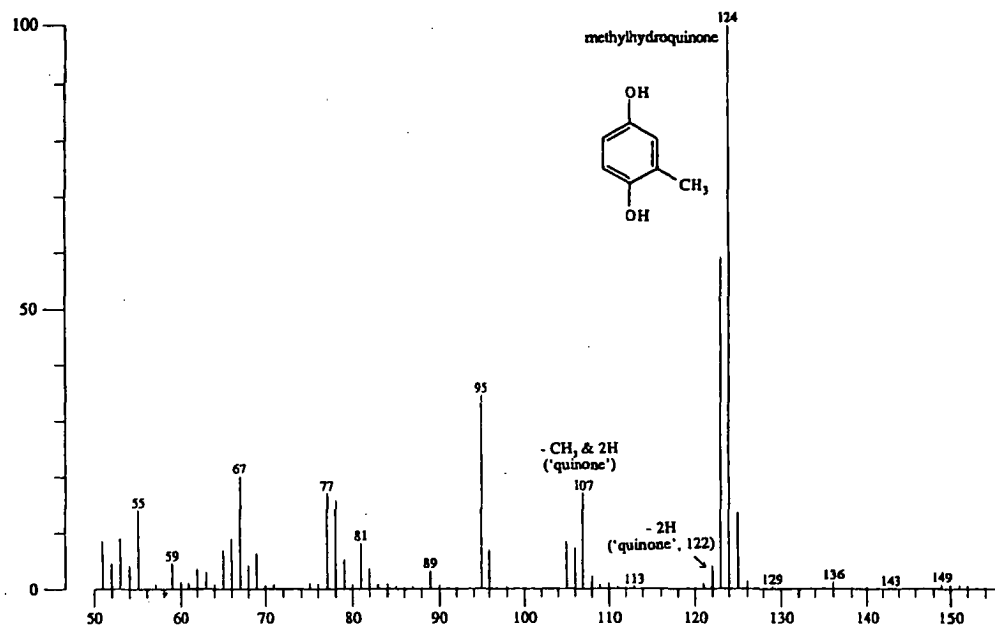




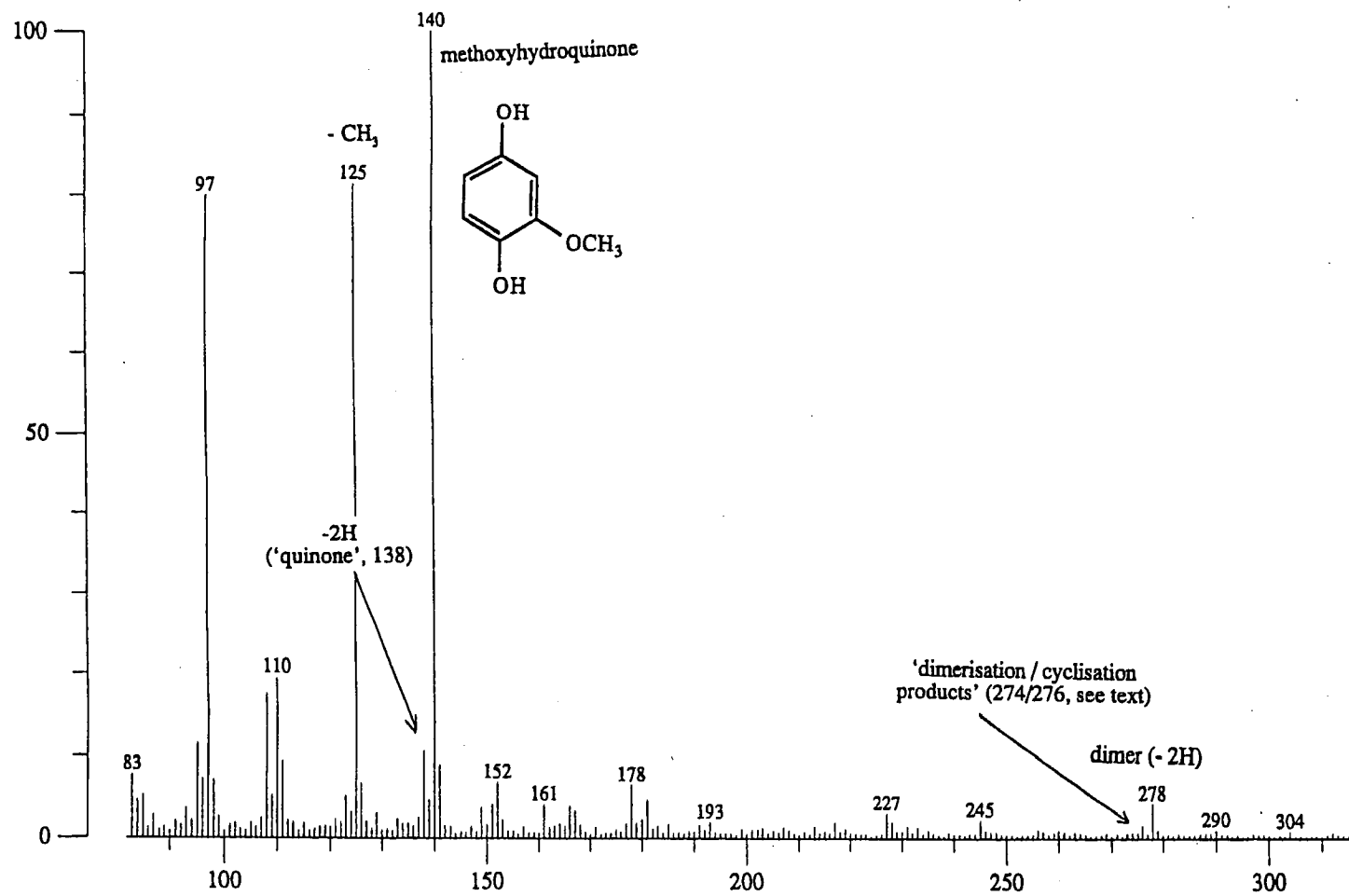
A5. Gas chromatography - mass spectra for irradiated vanillin.



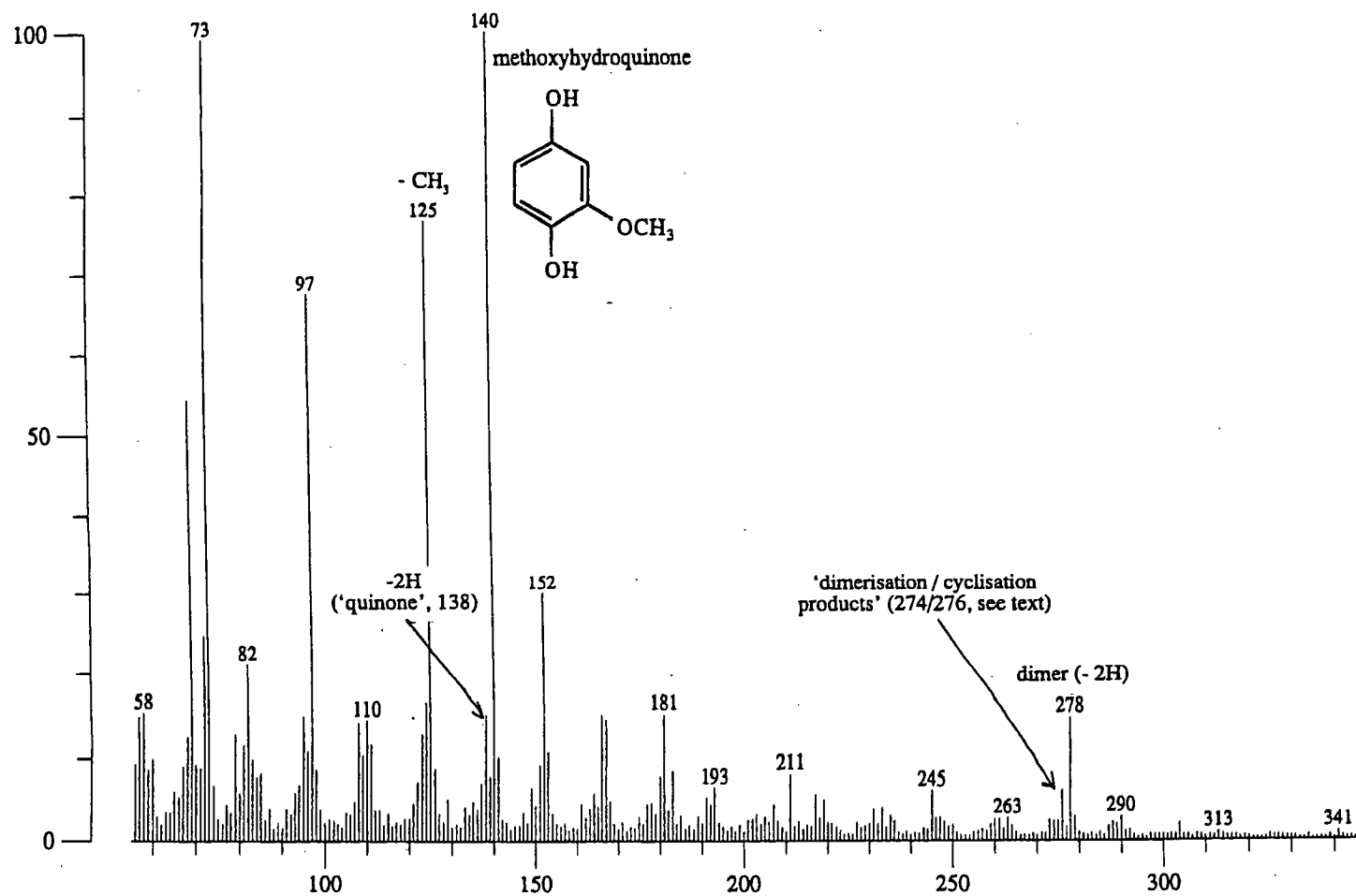
A6. Gas chromatography - mass spectra for irradiated methylhydroquinone.



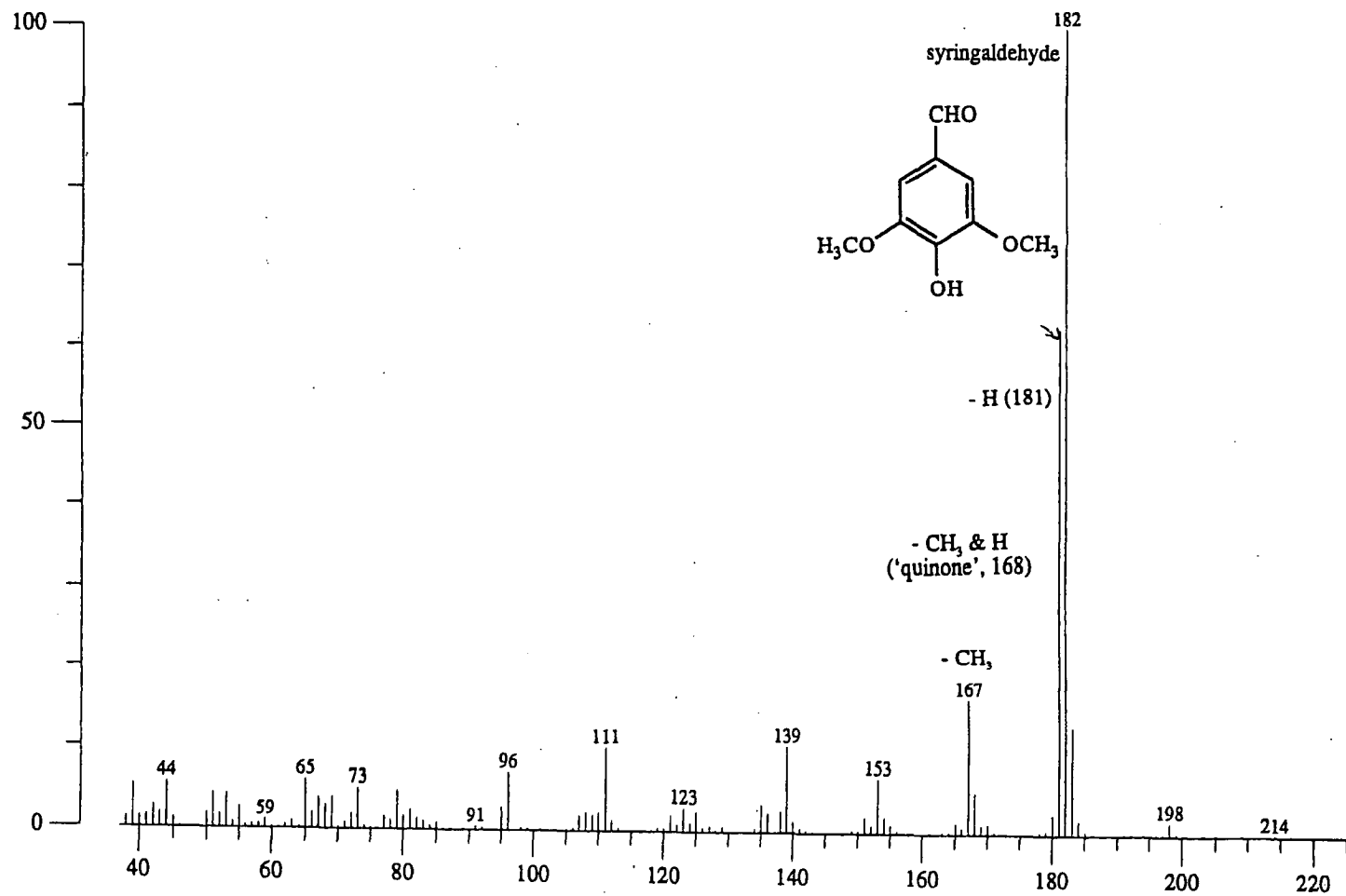
A7. Gas chromatography - mass spectra for irradiated methoxyhydroquinone.



**A7a.** Gas chromatography - mass spectra for *non-irradiated* methoxyhydroquinone.

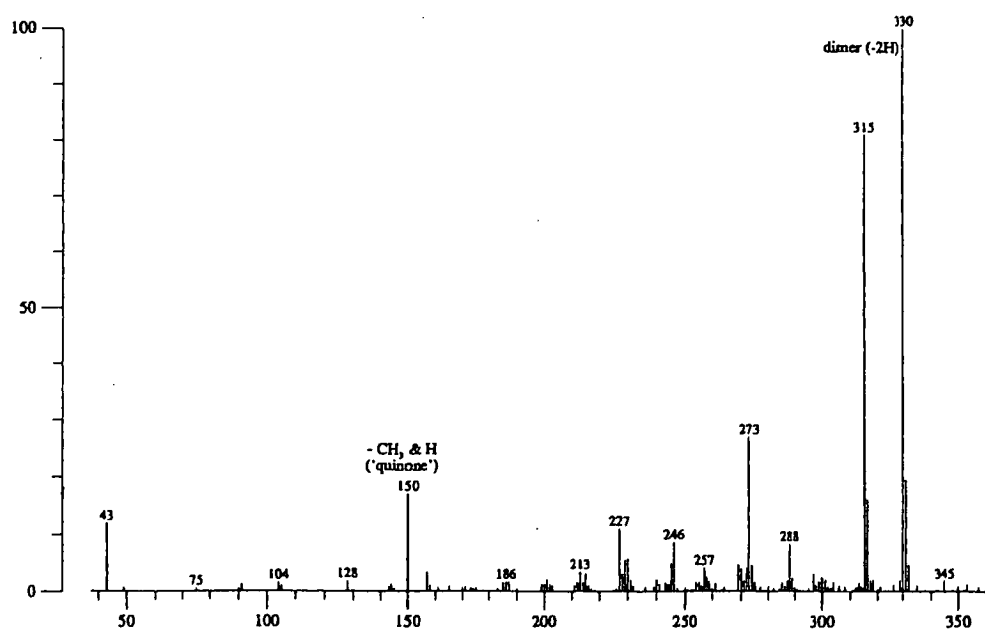
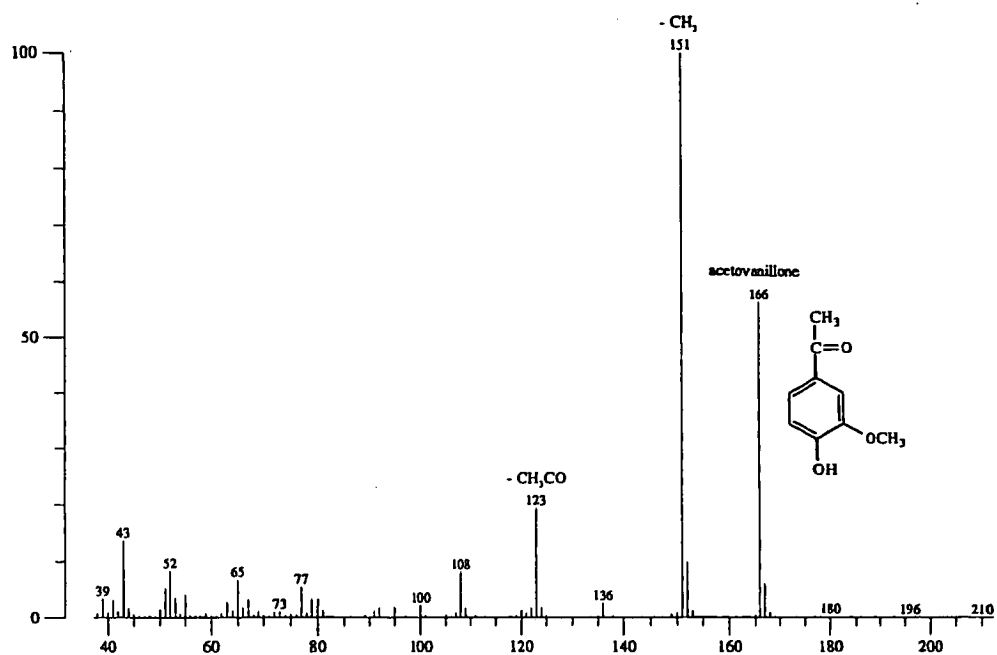


**A8. Gas chromatography - mass spectra for irradiated syringaldehyde.**





# A9. Gas chromatography - mass spectra for irradiated acetovanillone.

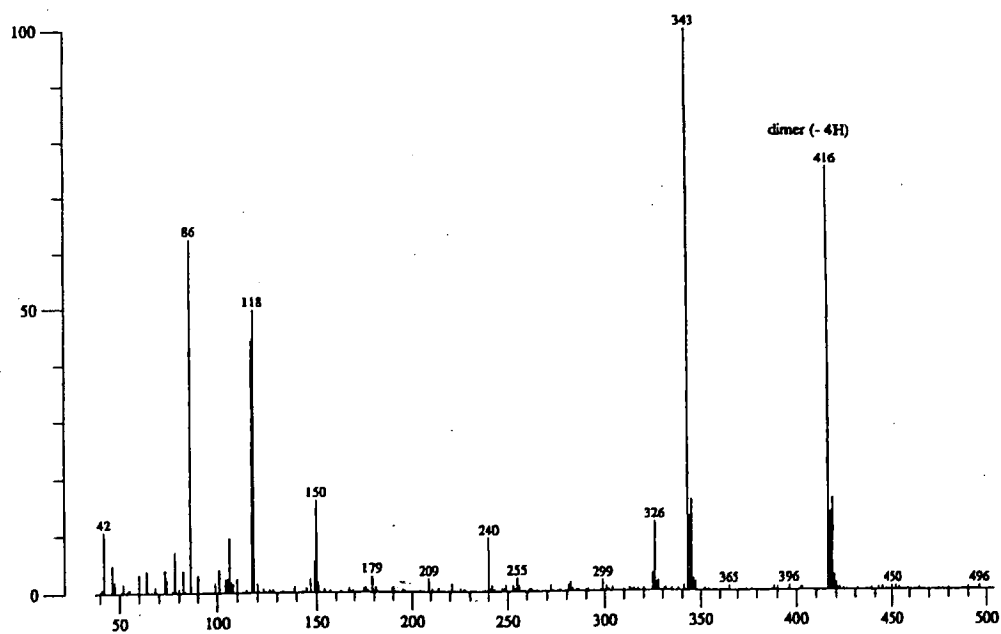
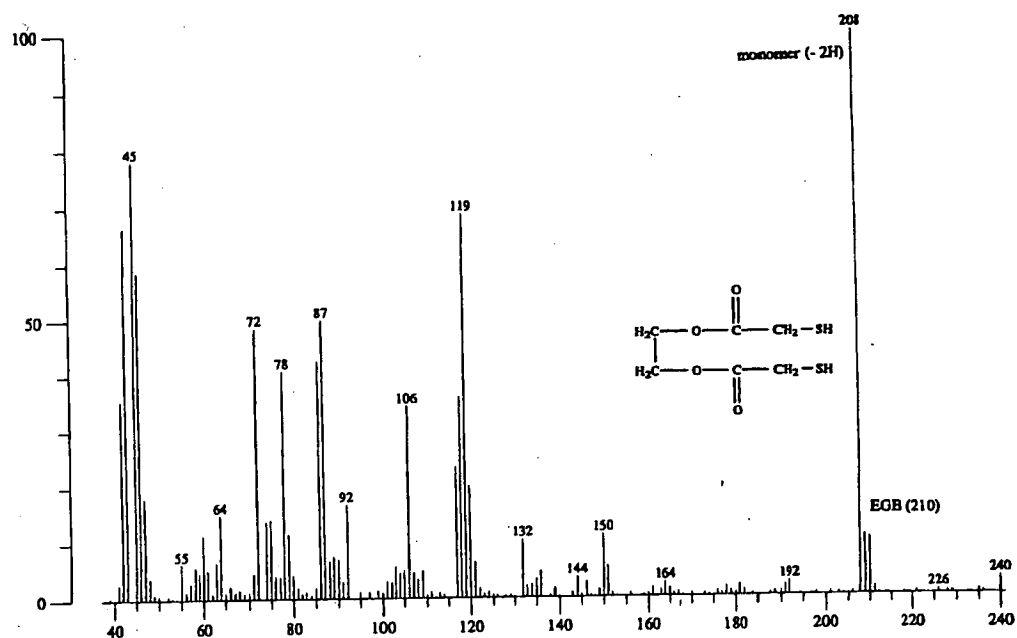


## **APPENDIX B**

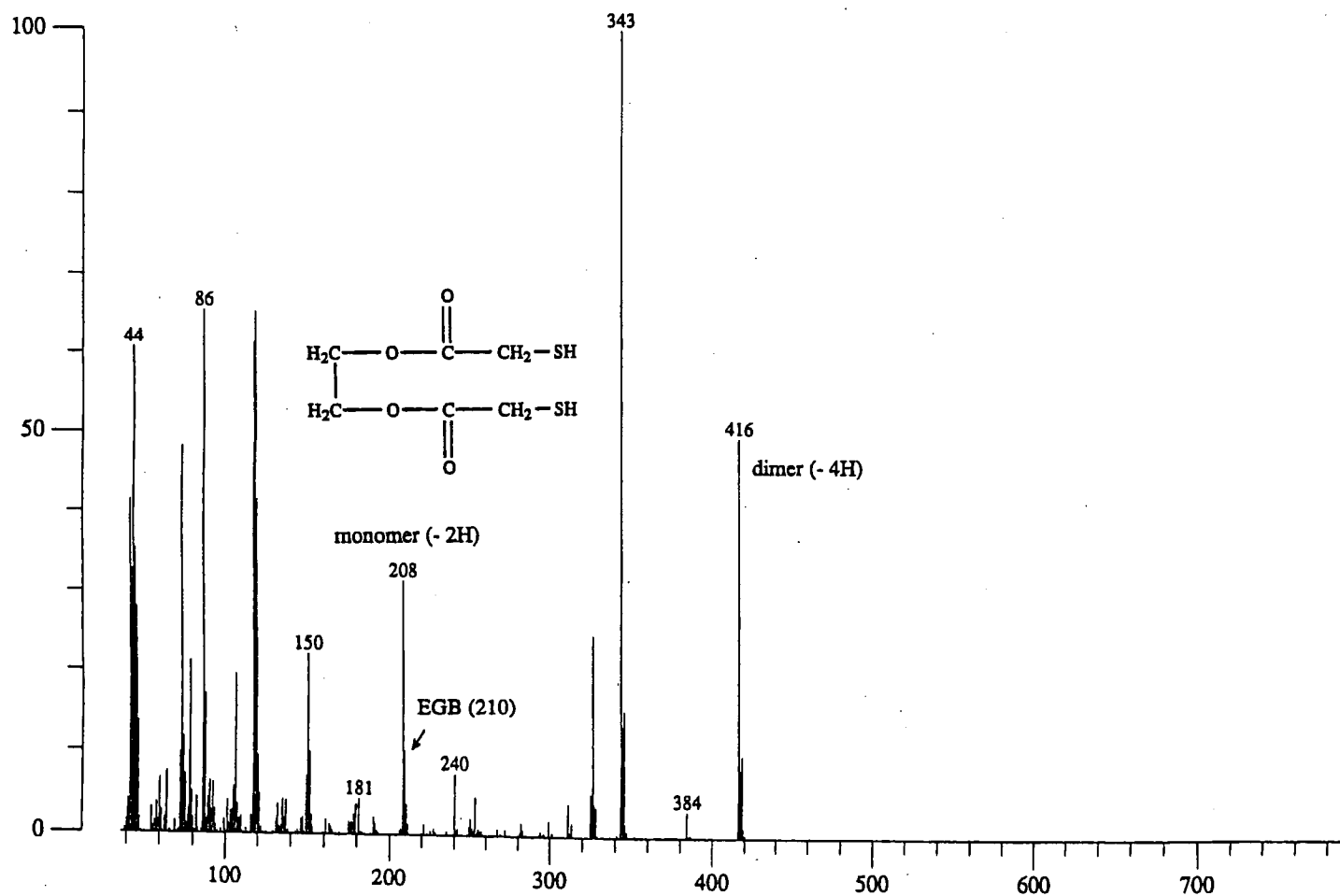
### **Gas Chromatography - Mass Spectra for Mercaptans which have been Irradiated, Heated, or Both**

(referenced in Chapters 5 and 6)

**B1. Gas chromatography - mass spectra for irradiated ethylene glycol bisthioglycolate (EGB).**

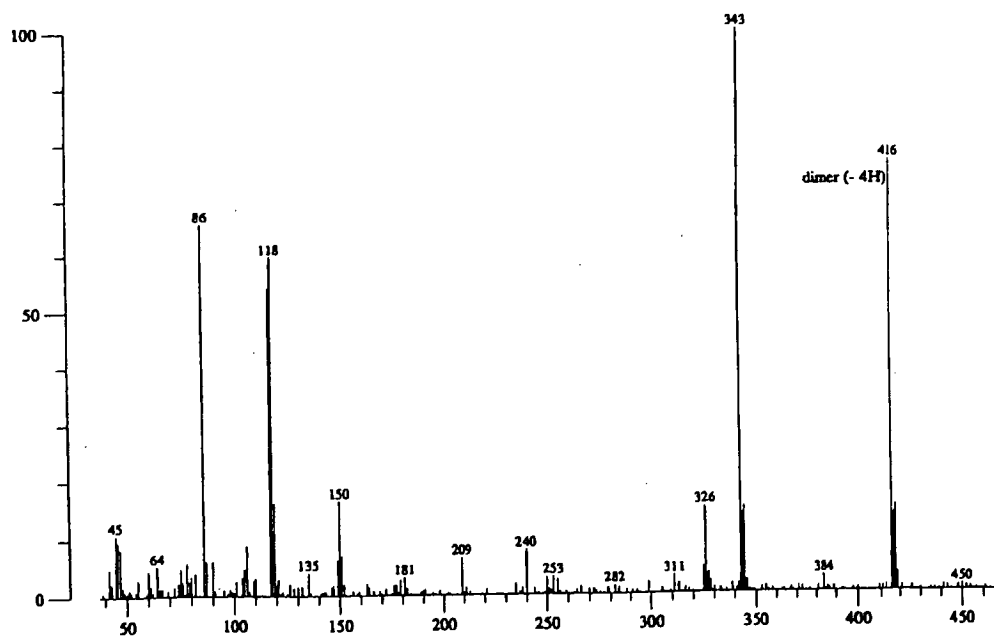
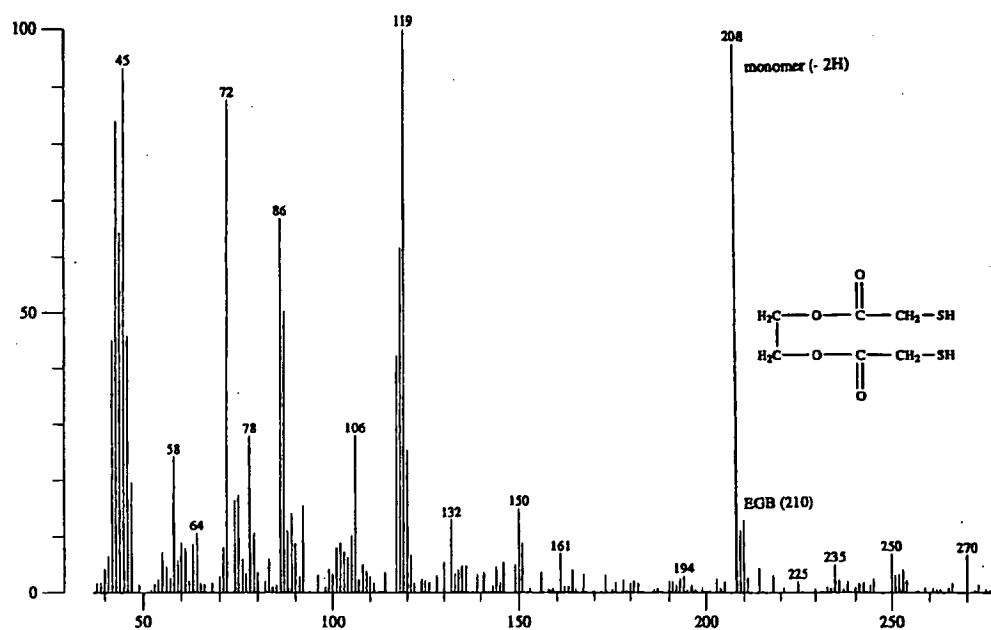


**B1a.** Gas chromatography - mass spectra for *non-irradiated* ethylene glycol bisthioglycolate (EGB).



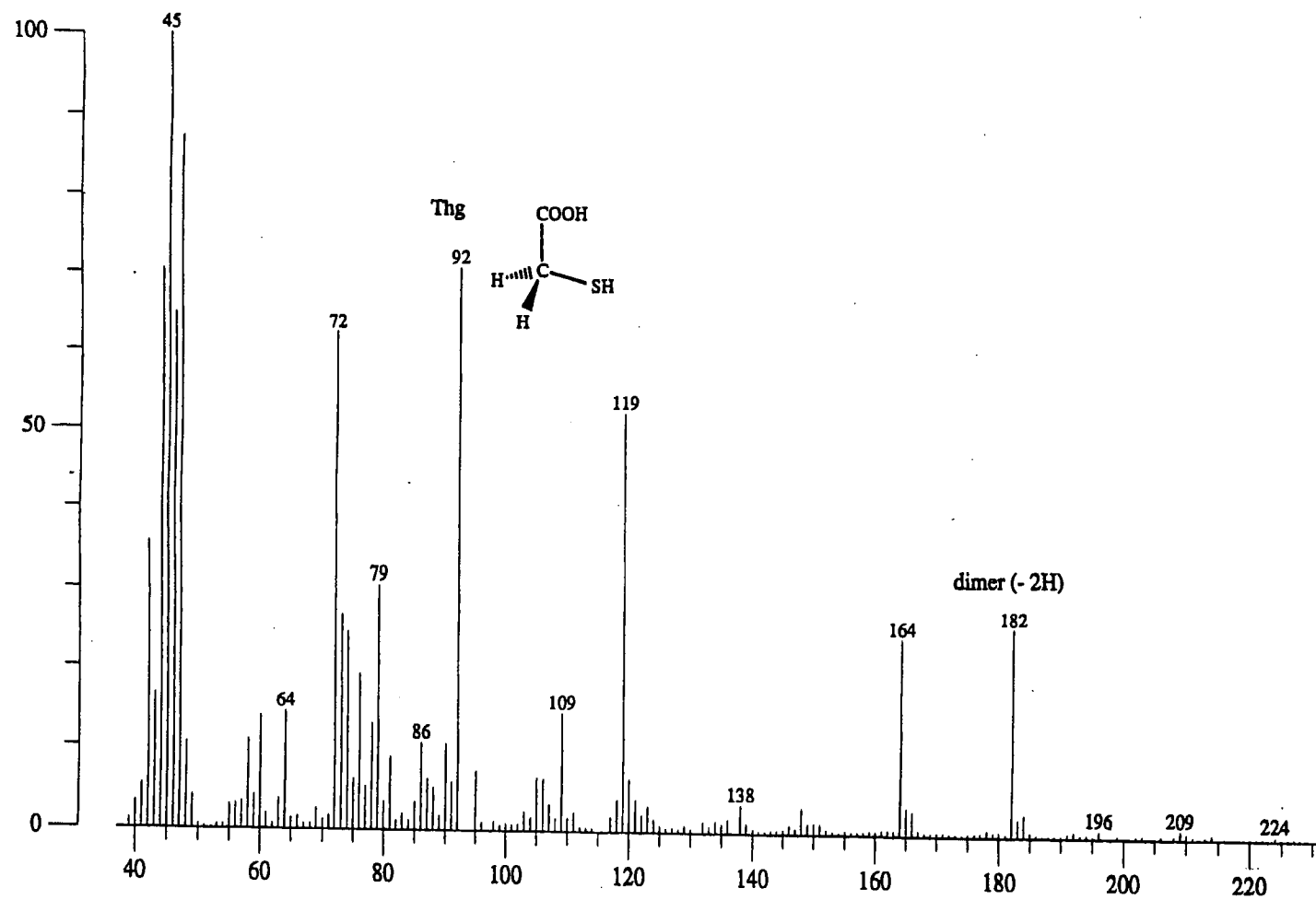


**B3. Gas chromatography - mass spectra for ethylene glycol bisthioglycolate (EGB)**  
 irradiated in the presence of heat.

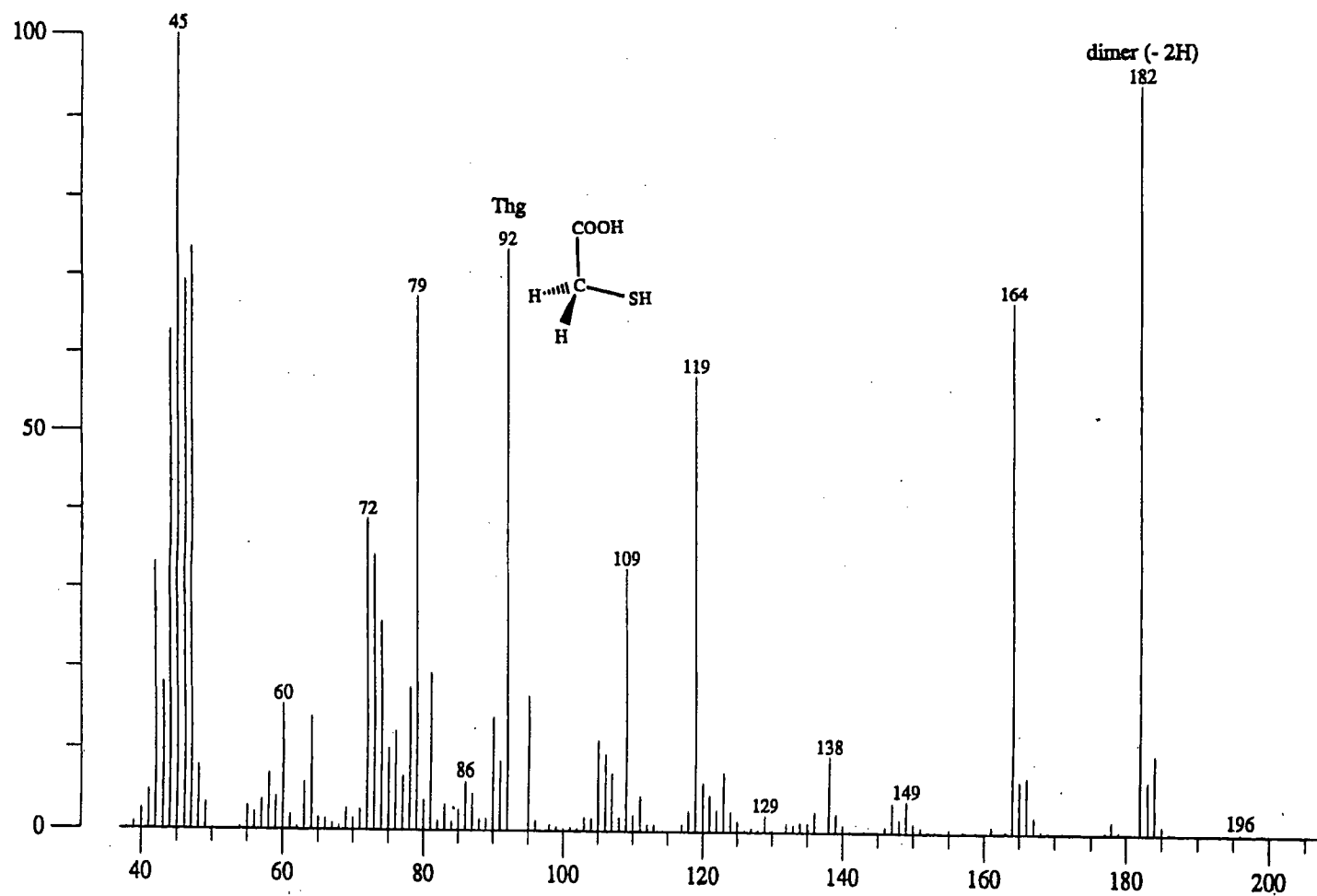




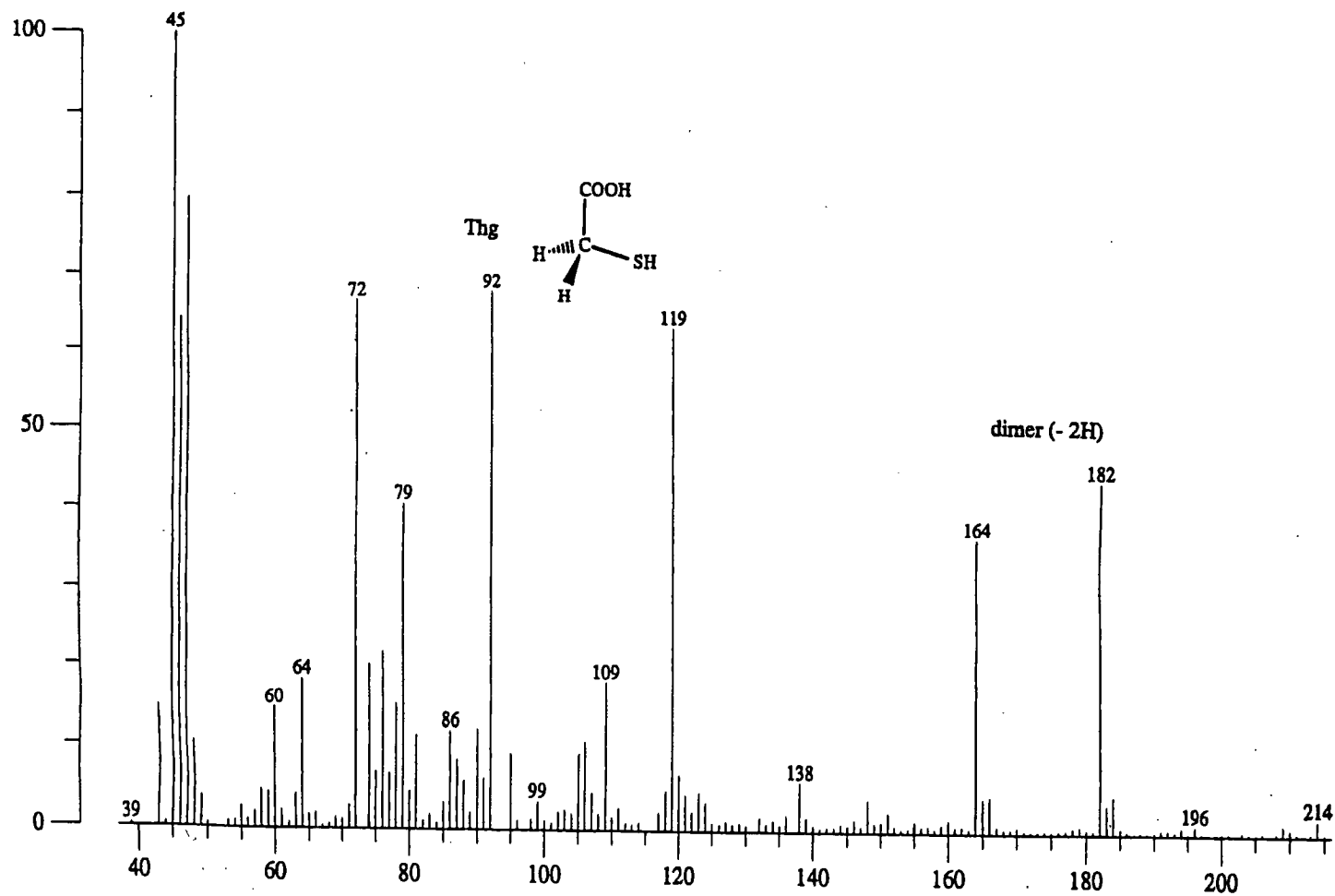
**B4.** Gas chromatography - mass spectra for irradiated thioglycolic acid (Thg).



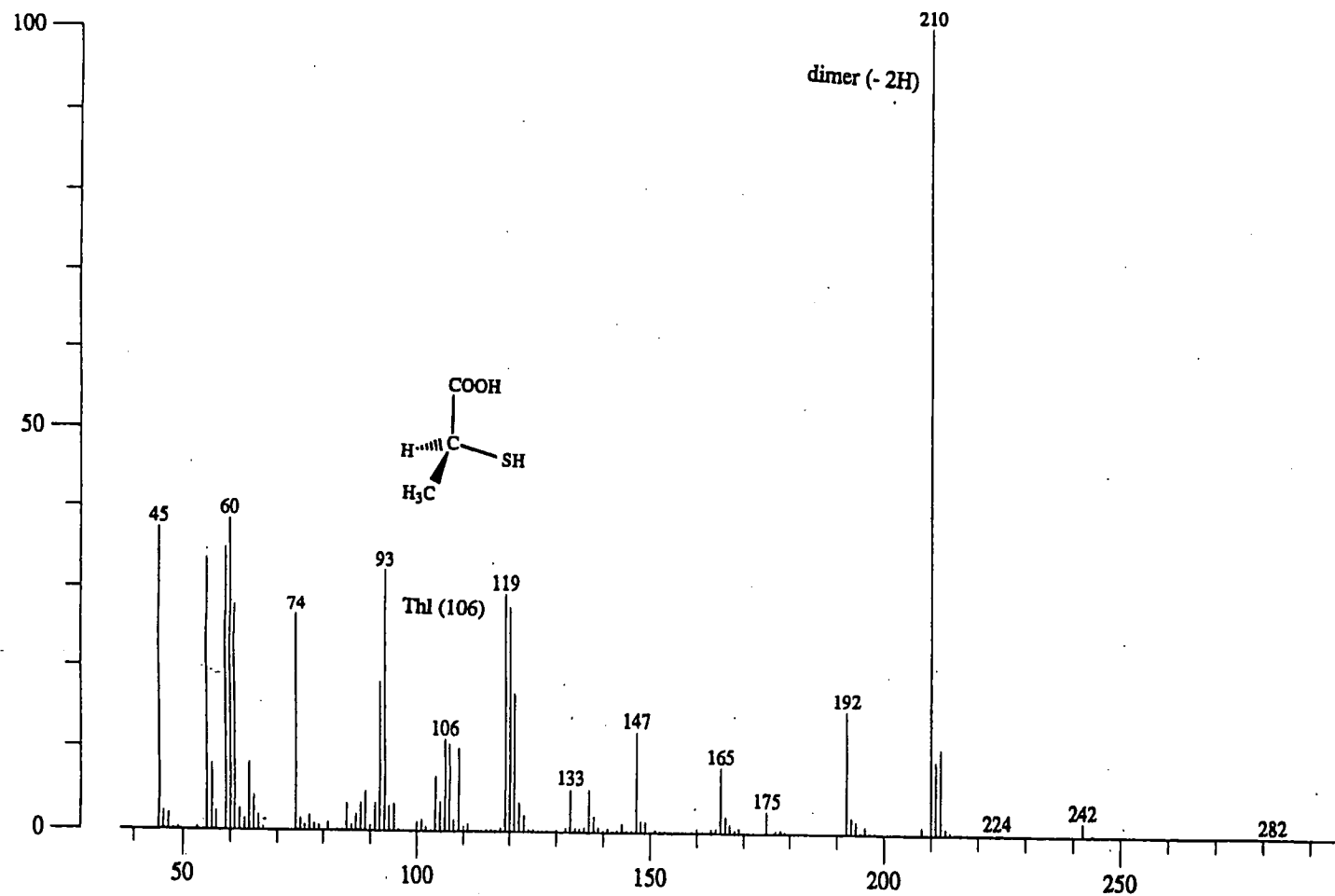
**B5. Gas chromatography - mass spectra for heated thioglycolic acid (Thg).**



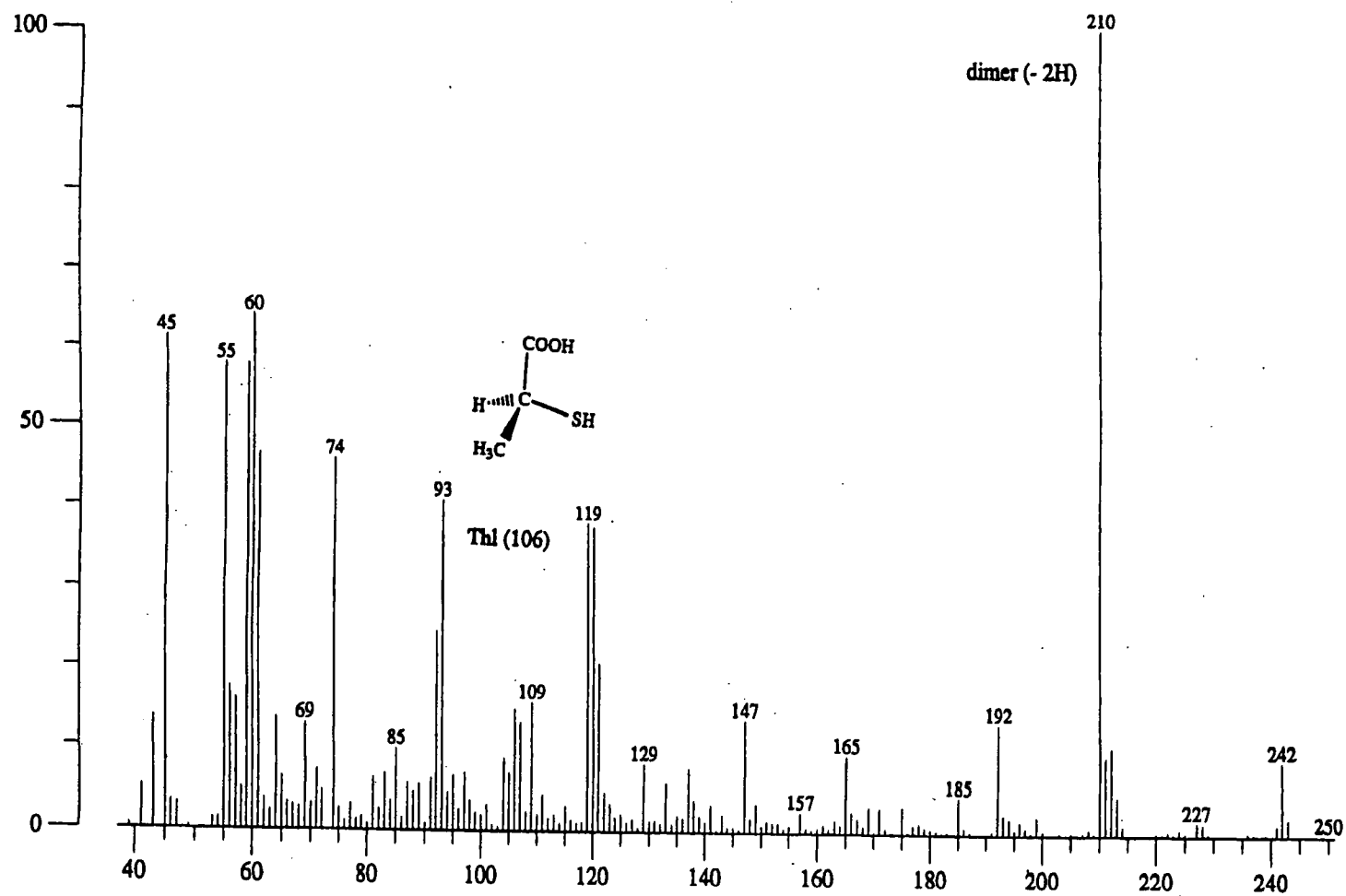
**B6. Gas chromatography - mass spectra for thioglycolic acid (Thg) irradiated in the presence of heat.**



**B7. Gas chromatography - mass spectra for irradiated thiolactic acid (Thl).**



**B8.** Gas chromatography - mass spectra for heated thiolactic acid (Thl).



**B9. Gas chromatography - mass spectra for thiolactic acid (Thl) irradiated in the presence of heat.**

